

# Thermolysis of waste plastics to liquid fuel

## A suitable method for plastic waste management and manufacture of value added products—A world prospective

Achyut K. Panda<sup>a,b,\*</sup>, R.K. Singh<sup>a,1</sup>, D.K. Mishra<sup>b,2</sup>

<sup>a</sup> Department of Chemical Engineering, National Institute of Technology, Rourkela, Orissa, India

<sup>b</sup> Jagannath Institute for Technology and Management, Parlakhemundi, Orissa, India

### ARTICLE INFO

#### Article history:

Received 16 April 2009

Accepted 6 July 2009

#### Keywords:

Sustainable development  
Alternate/renewable energy  
Plastics waste  
Waste-to-energy  
Fuel  
Value added products

### ABSTRACT

The present rate of economic growth is unsustainable without saving of fossil energy like crude oil, natural gas or coal. Thus mankind has to rely on the alternate/renewable energy sources like biomass, hydropower, geothermal energy, wind energy, solar energy, nuclear energy, etc. On the other hand, suitable waste management strategy is another important aspect of sustainable development. The growth of welfare levels in modern society during the past decades has brought about a huge increase in the production of all kinds of commodities, which indirectly generate waste. Plastics have been one of the materials with the fastest growth because of their wide range of applications due to versatility and relatively low cost. Since the duration of life of plastic products is relatively small, there is a vast plastics waste stream that reaches each year to the final recipients creating a serious environmental problem. Again, because disposal of post consumer plastics is increasingly being constrained by legislation and escalating costs, there is considerable demand for alternatives to disposal or land filling. Advanced research in the field of green chemistry could yield biodegradable/green polymers but is too limited at this point of time to substitute the non-biodegradable plastics in different applications. Once standards are developed for degradable plastics they can be used to evaluate the specific formulations of materials which will find best application in this state as regards their performance and use characteristics. Among the alternatives available are source reduction, reuse, recycling, and recovery of the inherent energy value through waste-to-energy incineration and processed fuel applications. Production of liquid fuel would be a better alternative as the calorific value of the plastics is comparable to that of fuels, around 40 MJ/kg. Each of these options potentially reduces waste and conserves natural resources. Plastics recycling, continues to progress with a wide range of old and new technologies. Many research projects have been undertaken on chemical recycling of waste plastics to fuel and monomer. This is also reflected by a number of pilot, demonstration, and commercial plants processing various types of plastic wastes in Germany, Japan, USA, India, and elsewhere. Further investigations are required to enhance the generation of value added products (fuel) with low investments without affecting the environment. The paper reviews the available literature in this field of active research and identifies the gaps that need further attention.

© 2009 Elsevier Ltd. All rights reserved.

### Contents

1. Statistics of consumption of plastics and generation of plastics waste.....	234
2. Sources and properties of plastic wastes .....	235
2.1. Municipal plastic wastes .....	235
2.2. Industrial plastic wastes.....	235
3. Different methods of plastic waste management.....	235
3.1. Land filling .....	236
3.2. Mechanical recycling .....	236

\* Corresponding author at: Department of Chemical Engineering, National Institute of Technology, Rourkela 769008, Orissa, India. Tel.: +91 09437132916.

E-mail addresses: [achyut.panda@rediffmail.com](mailto:achyut.panda@rediffmail.com) (A.K. Panda), [rksingh@nitrrkl.ac.in](mailto:rksingh@nitrrkl.ac.in), [raghubansh.singh@rediffmail.com](mailto:raghubansh.singh@rediffmail.com) (R.K. Singh), [ghanadam@gmail.com](mailto:ghanadam@gmail.com) (D.K. Mishra).

<sup>1</sup> Tel.: +91 661 2462260 (O); +91 661 2463260 (R).

<sup>2</sup> Tel.: +91 674 2394074.

3.3.	Biological recycling .....	237
3.4.	Thermal recycling/incineration .....	237
3.5.	Chemical recycling .....	237
3.5.1.	Depolymerisation .....	237
3.5.2.	Partial oxidation .....	237
3.5.3.	Cracking/pyrolysis .....	237
4.	Pyrolysis of plastic waste to liquid fuel—the process .....	238
4.1.	Thermal pyrolysis of polyolefins .....	238
4.2.	Catalytic cracking of polyolefins .....	238
4.2.1.	The hydrocarbon cracking mechanism .....	239
4.3.	Process design .....	240
4.3.1.	Effect of feed composition (type of polymer) on product yield and distribution .....	240
4.3.2.	Effect of catalyst loading .....	241
4.3.3.	Effect of catalyst contact mode .....	243
4.3.4.	Effect of particle/crystallite size of catalyst on product distribution .....	243
4.3.5.	Effect of reactor type .....	243
4.3.6.	Effect of other process parameters .....	244
5.	Economic and ecological aspects of catalytic pyrolysis of plastics .....	244
6.	Future works .....	245
7.	Conclusion .....	245
	References .....	246

## 1. Statistics of consumption of plastics and generation of plastics waste

Plastics are “one of the greatest innovations of the millennium” and have certainly proved their reputation to be true. There are a numerous ways that plastic is and will be used in the years to come. The fact that plastic is lightweight, does not rust or rot, low cost, reusable and conserves natural resources is the reason for which plastic has gained this much popularity. Again, Plastics save energy and CO<sub>2</sub> emissions during their use phase. If we were to substitute all plastics in all applications with the prevailing mix of alternative materials, and look from a life cycle perspective, then 22.4 million additional tons of crude oil per year would be required [1]. Constant developments in polymer technology, processing machineries, know-how and cost effective production is fast replacing conventional materials in every segment with plastics.

Continuous innovation explains that, plastics production has increased by an average of almost 10% every year on a global basis since 1950. The total global production of plastics has grown from around 1.3 million tonnes (MT) in 1950 to 245 MT in 2006. Plastics continue to be a global success story with Europe (EU25 + Norway (NO) and Switzerland (CH) remaining a major manufacturing region, producing about 25% of the total estimated worldwide plastics production of 245 million tonnes during 2006. An analysis of plastics consumption on a per capita basis shows that this has now grown to over 100 kg/y in North America and Western Europe, with the potential to grow to up to 130 kg/y per capita by 2010 [1]. The highest consumption of plastics among different countries is found in USA which is equal to 27.3 MT against 170 MT world consumption in 2000 and is expected to reach to 39 MT by 2010 [2]. The highest potential for growth can be found in the rapidly developing parts of Asia (excluding Japan), where currently the per capita consumption is only around 20 kg/year. In the European context, it is the new member states such as Poland, Czech Republic and Hungary which are expected to see the biggest increase as their economies development. Their current average per capita consumption of 55 kg is a little more than half of that of the old Member State. Significant growth rate in Asia and Eastern Europe expected, however in 2010 demand per capita in Asia and Eastern Europe is still much below the rate of the “traditional markets” like America and Western Europe. The average Indian consumption of virgin plastics per capita reached 3.2 kg in 2000/2001 (5 kg if recycled material is included) from a mere 0.8 kg in

1990/1991 and 1.8 kg in 1998/1999. However, this is only one-fourth of the consumption in China (12 kg/capita, 1998) and one sixth of the world average (18 kg/capita) [3,4]. The Fig. 1 gives the comparison of per capita consumption of plastics over three different periods. This plot represents a clear picture of growth of plastic consumption in world.

The growth of the Indian plastic industry has been phenomenal equal to 17% is higher than for the plastic industry elsewhere in the world [5]. India has a plastic consumption of 3.2 MT during 2000 and is expected to reach nearly 12.5 MT by 2010 [2,3]. Hindu Business line, January 21, 2006 reveals India will be the third largest plastics consumer by 2010 after USA and China. The reason of highest growth rate in last few year in India is due to the fact that, one third of the population is destitute and may not have the disposable income to consume much in the way of plastics or other goods. The virgin industry does not target this population to expand its markets. However, one third of the population is the middle class whose aspirations could be moulded to increase consumption. Plastic manufacturers create needs for this segment of population. The rising needs of the middle class, and abilities of plastics to satisfy them at a cheaper price as compared to other materials like glass and metal, has contributed to an increase in the consumption of plastics in the last few years [5].

The rapid rate of plastic consumption throughout the world has led to the creation of increasing amounts of waste and this in turn poses greater difficulties for disposal. This is due to the fact that duration of life of plastic wastes is very small (roughly 40% have duration of life smaller than 1 month) [6] and depending on the area of application, the service life of plastic products ranges from 1 to 35 years [3]. The weighted average service life of all plastics products is different in different countries and in India it is 8 years; this is much less than the weighted average service life for Germany which is estimated at 14 years. This difference in service life reflects the fact that a particularly high share of plastics is used for short life products in India (e.g. share of plastics packaging: 42% in India versus 27% in Germany [3]).

Plastic in municipal solid waste streams make up only 7–9% of the weight of the total waste stream, by volume they may represent 20–30%. Of the organic waste stream, that is, after removal of glass, metals, etc., plastics are about 9–12% by weight [7]. In addition to the presence of plastics in municipal waste streams, many wastes collected from manufacturing or service industries may contain much higher proportions of plastics.

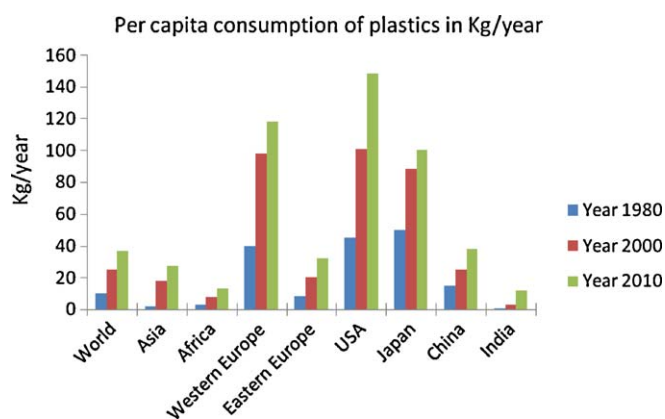


Fig. 1. Comparison of per capita consumption of plastics over three different periods.

According to estimates, in Europe plastic wastes represent 15–25% of municipal waste. The amount of plastic materials in Europe was 30 MT during 2000 and it will reach 35 MT by 2010 [8]. In USA the amount of plastic waste was 24.8 MT in 2000 and 29.7 MT in 2006. The amount of plastic consumed as a percentage of total waste has increased from less than 1% in 1960 to 11.7% in 2006 (Environmental Protection Agency (EPA) report 2000 and 2006). In Japan, 15 MT of plastics are produced annually and 10 MT of plastics are discarded [9]. Similarly in India the amount of plastic waste during 2000/2001 was 2.38 MT and is estimated to rise to more than 8 MT by 2010 and 20 MT by 2030 [3].

Plastics have become a major threat due to their non-biodegradability and high visibility in the waste stream. Littering also results in secondary problems such as clogging of drains and animal health problems. Their presence in the waste stream poses a serious problem when there is lack of efficient end of life management of plastic waste. Some countries have too much of plastic rubbish for them to dispose off that, due to the high cost of the disposal of the plastic rubbish, many resort to indiscriminate dumping of plastics. Plastic waste has attracted widespread attention in India, particularly in the last five years, due to the widespread littering of plastics on the landscape of India. The environmental issues due to plastic waste arise predominantly due to the throwaway culture that plastics propagate, and also the lack of an efficient waste management system [5].

## 2. Sources and properties of plastic wastes

Plastic wastes can be classified as industrial and municipal plastic wastes according to their origins; these groups have different qualities and properties and are subjected to different management strategies [10]. Plastic wastes represent a considerable part of municipal wastes; furthermore huge amounts of plastic waste arise as a by-product or faulty product in industry and agriculture [8]. Of the total plastic waste, over 78 wt% of this total corresponds to thermoplastics and the remaining to thermosets [6]. Thermoplastics are composed of polyolefins such as polyethylene, polypropylene, polystyrene and polyvinyl chloride [11] and can be recycled. On the other hand thermosets mainly include epoxy resins and polyurethanes and cannot be recycled [6].

### 2.1. Municipal plastic wastes

Municipal plastic wastes (MSW) normally remain a part of municipal solid wastes as they are discarded and collected as household wastes. The various sources of MSW plastics includes domestic items (food containers, packaging foam, disposable cups, plates, cutlery, CD and cassette boxes, fridge liners, vending cups,

electronic equipment cases, drainage pipe, carbonated drinks bottles, plumbing pipes and guttering, flooring, cushioning foams, thermal insulation foams, surface coatings, etc.), agricultural (mulch films, feed bags, fertilizer bags, and in temporary tarpaulin-like uses such as covers for hay, silage, etc.), wire and cable, automobile wrecking, etc. Thus, the MSW collected plastics waste is mixed one with major components of polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyethylene terephthalate, etc. The percentage of plastics in MSW has increased significantly [10]. Waste plastics amount to around 20% of the volume and 8% of the weight of all MSW in USA during 2000 which increased to 11.7% by 2006 (Environmental Protection Agency (EPA) 2006 reports) and in Europe it is 15–25% (2004) [8]. In China (2000) and Japan (2001) plastics constitute 13% and 7% respectively in MSW [12,13]. Similarly in India, of the total MSW, plastic waste increased from 0.7% in 1971 to 4% in 1995 and 9% in 2003 [3,4].

In order to recycle municipal plastic wastes, separation of plastics from other household wastes is required. For mixed plastics some mechanical separation equipment is currently available [14,15]. For example, using a wet separation process mixed plastics can be separated into two groups: those with a density greater than water such as polystyrene and polyvinyl chloride, and those with a density lower than that of water such as polyethylene, polypropylene, and expanded polystyrene. The latter group is much larger than the first group. Consequently, recycling of municipal plastic wastes should deal with plastic mixtures of polyethylene, polypropylene and polystyrene, provided that the above separation procedures are practiced. Although MSW separation technologies have been studied extensively, it is still not possible to classify MSW mechanically and obtain marketable fractions. So waste separation at the household would be a better option with where household wastes are separately disposed into three parts: (i) combustibles such as paper, kitchen waste, textiles, and wood, (ii) incombustibles such as metals, glass, ceramics, and (iii) plastics [10].

### 2.2. Industrial plastic wastes

Industrial plastic wastes (so-called primary Waste) are those arising from the large plastics manufacturing, processing and packaging industry. The industrial waste plastic mainly constitute plastics from construction and demolition companies (e.g. polyvinyl chloride pipes and fittings, tiles and sheets) electrical and electronics industries (e.g. switch boxes, cable sheaths, cassette boxes, TV screens, etc.) and the automotive industries spare-parts for cars, such as fan blades, seat coverings, battery containers and front grills). Most of the industrial plastic waste have relatively good physical characteristics i.e. they are sufficiently clean and free of contamination and are available in fairly large quantities. It has been exposed to high temperatures during the manufacturing process which may have decreased its characteristics, but it has not been used in any product applications.

Municipal plastic wastes are heterogeneous, where as industrial plastics wastes are homogeneous in nature. For homogeneous plastic wastes, repelletization and remolding seem to be a simple and effective means of recycling. But when plastic wastes are heterogeneous or consist of mixed resins, they are unsuitable for reclamation. In this case thermal cracking into hydrocarbons may provide a suitable means of recycling, which is termed chemical recycling [10].

## 3. Different methods of plastic waste management

Due to population increase, the demand for plastic products has steadily increased over the last 40 years. Since plastics are

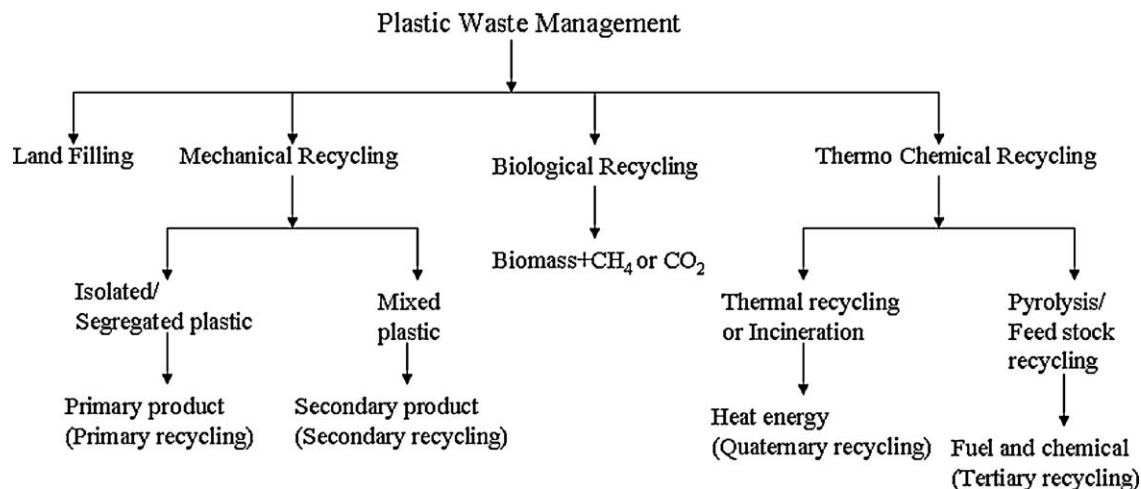


Fig. 2. Different routes for plastic waste management.

non-biodegradable, they cannot be easily returned to the natural carbon cycle; hence the life cycle of plastic materials ends at waste disposal facilities [16]. There are several methods for disposal of municipal and industrial plastic waste, i.e. landfill, incineration (energy recovery), true material recycling (similar recycled product or monomer recovery), and chemical recovery [17]. The suitable treatment of plastic wastes is one of the key questions of the waste management and is important from energetic, environmental, economical and political aspects [18]. In most developed societies domestic organic waste, including plastics packaging, is disposed of in sanitary land filled or by incineration [17]. During early 2000, the largest amount of plastic wastes is disposed of by land filling (65–70%), and incineration (20–25%). Recycling is only about 10% [10]. This figure varies from country to country, however they are approximately nearer to it with some exception. In Japan, the percentage of municipal plastic wastes, as a fraction of MSW, that was land filled in the early 1980s was estimated to be 45%, incineration was 50%, and the other 5% was subjected to separation and recycling. In the USA, more than 15% of the total MSW was incinerated in 1990; only about 1% of post-consumer plastics were recycled. In India, during 1998 around 800,000 tonnes representing 60% of plastic wastes generated in India was recycled involving 2000 units. This level of recycling is the highest in the world. The corresponding figure for Europe is 7%, Japan 12%, China 10%, and South Africa 16% (Central Pollution Control Board, India, figures—1998). In Europe 2006 marks a milestone as the first year when recovery and disposal rates of used plastic were equal. The recovery rate of post-consumer end-of-life plastics now stands at 50% and disposal stands at 50%. The recycling rate for post-consumer plastics has increased to 19.7% up from 18% in 2005 and energy recovery has increased to 30.3% up from 29% in 2005. Of the 11.5 million tonnes recovered 4.5 million tonnes were recycled as material and feedstock and 7.0 million tonnes were recovered as energy. The overall material recycling rate of post-consumer plastics in 2006 was 19.7%, with mechanical recycling at 19.1% (up 2.5% point over 2005) and feedstock recycling at 0.6% (down 1% from 2005). The energy recovery rate was up by 1.5% from 2005 to 30.3%, reflecting the stricter legislation on landfill in several Member States [1]. From the above recent data it is clear that there is increase in the recycling operation (material and energy) compared land filling due to strict regulations and growing awareness.

The Fig. 2 represents the different routes for plastic waste management being followed.

### 3.1. Land filling

Highest portion of the solid waste including plastics have been subjected to landfill. However, disposing of the waste to landfill is becoming undesirable due to legislative pressures (where waste to landfill must be reduced by 35% over the period from 1995 to 2020), rising costs, the generation of explosive greenhouse gases (such as methane) and the poor biodegradability of commonly used packaging polymers [19]. In light of these hazards, the EPA has improved federal regulations for land filling by normalizing the use of liners in the landfill bed, ground water testing for waste leaks, and post landfill closure care; however, since waste plastics have a high volume to weight ratio, appropriate landfill space is becoming both scare and expensive. So, the other methods outlined in Fig. 2 should be preferred as an alternative waste management procedure to replace land filling.

### 3.2. Mechanical recycling

Mechanical recycling is reprocessing of the used plastics to form new similar products. This is a type of primary and secondary recycling of plastic where the homogeneous waste plastics are converted into products with nearly same or less performance level than the original product. Efforts were made by the polymer technologists in the 1970s to recover materials from waste plastics suitable for second use but practical experience has shown that reprocessing of mixed contaminated plastics produces polymer polyblends that are inferior mechanically and lacking in durability (which is explained due to peroxidation) compared with those produced from virgin polymers [20]. Although at first sight mechanical recycling of plastic wastes appears to be a 'green' operation, the re-processing operation is not cost effective as it needs high energy for cleaning, sorting, transportation and processing in addition to the additives used to provide a serviceable product [21]. Again, materials recycling of household waste plastics is particularly difficult when they are contaminated with biological residues or, as is usually the case, when they are a mixture of different kinds of plastics. Technology is being introduced to sort plastics automatically, using various techniques such as X-ray fluorescence, infrared and near infrared spectroscopy, electrostatics and flotation. However the economic viability and practicability of such process in industrial application is not apparent [27]. Entrepreneurial effort has gone into the development of special processing equipment to convert mixed plastics wastes to wood or concrete substitutes in the manufacture of fence



posts, benches, boat docks, etc., but there are serious doubts about the ecological benefits of doing this. Some limited success has been achieved with mixed plastics wastes in the manufacture of plastics-based underground chambers by increasing wall dimensions to match the load-bearing strength of concrete. In this application, there is no significant long term deterioration due to exposure to the weather but this procedure could never utilise more than a small fraction of the mixed polymer wastes available [22]. Considerable academic interest has centered round the use of 'compatibilizers' (more correctly, solid phase dispersants) to upgrade the mechanical performance of mixed plastics polyblends but in general this is an expensive and energy-intensive procedure which cannot be justified for domestic mixed plastics wastes [20,21]. In this way, it is apparent that mechanical recycling, although employed widely, is not a suitable method when the quality of secondary produce and ecological aspects are considered.

### 3.3. Biological recycling

Both natural and synthetic cis-poly (isoprene) become highly resistant to bio-degradation when made into industrial products (e.g. tyres) which is a direct consequence of the presence of highly effective antioxidants added during their manufacture [23]. This has led to intensive research both in industry and in universities to develop polymeric materials that conform to user requirements but are also returned to the biological cycle after use. This resulted in development of biodegradable polymers which can be converted back to the biomass in a realistic time period [24–26]. Biodegradable plastics are already being used successfully in different countries. Mostly they are introduced in food/catering industry which photo-degrades in six weeks. There is also potential to use such plastics in non-packaging applications such as computer or car components.

However, there are a number of concerns over the use of degradable plastics. First, these plastics will only degrade if disposed of in appropriate conditions. For example, a photodegradable plastic product will not degrade if it is buried in a landfill site where there is no light. Second, they may cause an increase in emissions of the greenhouse gas methane, as methane is released when materials biodegrade anaerobically. Third, the mixture of degradable and non-degradable plastics may complicate plastics sorting systems. Last but not least, the use of these materials may lead to an increase in plastics waste and litter if people believe that discarded plastics will simply disappear [27]. Due to all these problems at present the biodegraded plastics cannot substitute all the application areas of synthetic plastics.

### 3.4. Thermal recycling/incineration

Energy generation by incineration of plastics waste is in principle a viable use for recovered waste polymers since hydrocarbon polymers replace fossil fuels and thus reduce the CO<sub>2</sub> burden on the environment. Table 1 [20] shows that, the calorific value of polyethylene is similar to that of fuel oil and the

thermal energy produced by incineration of polyethylene is of the same order as that used in its manufacture. Incineration is the preferred energy recovery option of local authorities because there is financial gain by selling waste plastics as fuel [22]. Co-incineration of plastic wastes with other municipal solid wastes may be increasingly practiced, because the high caloric value of plastics can enhance the heating value of MSW and facilitate an efficient incineration, while their energy content can also be recovered.

However, in most developed countries public distrust of incineration at present limits the potential of waste-to-energy technologies as it produce greenhouse gases and some highly toxic pollutants such as polychlorinated dibenzo para dioxins (PCDD) and polychlorinated dibenzo furans (PCDF). The potential relationship between plastics fed into an incinerator and the formation of dioxins and furans is still unclear and has been suggested that the chlorine content in PVC and other plastics is related to the formation of dioxins and furans [28].

### 3.5. Chemical recycling

Current state of the art Feedstock recycling, also known as chemical recycling or tertiary recycling, aims to convert waste polymer into original monomers or other valuable chemicals. These products are useful as feedstock for a variety of downstream industrial processes or as transportation fuels. There are three main approaches: depolymerisation, partial oxidation and cracking (thermal, catalytic and hydrocracking).

#### 3.5.1. Depolymerisation

Condensation polymers which include materials such as polyamides, polyesters, nylons and polyethylene terephthalate can be depolymerised via reversible synthesis reactions to initial diacids and diols or diamines. Typical depolymerisation reactions such as alcoholysis, glycolysis and hydrolysis yield high conversion to their raw monomers. However, addition polymers which include materials such as polyolefins, typically making up 60–70% of municipal solid waste plastics, cannot be easily depolymerised into the original monomers by reverse synthesis reaction.

#### 3.5.2. Partial oxidation

The direct combustion of polymer waste, which has a good calorific value, may be detrimental to the environment because of the production of noxious substances such as light hydrocarbons, NO<sub>x</sub>, sulfur oxides and dioxins. Partial oxidation (using oxygen and/or steam), however, could generate a mixture of hydrocarbons and synthesis gas (CO and H<sub>2</sub>), the quantity and quality being dependent on the type of polymer used. A new type of waste gasification and smelting system using iron-making and steel-making technologies has been described by Yamamoto et al. [29], reportedly to produce a dioxin-free and high-calorie purified gas. Hydrogen production efficiency of 60–70% from polymer waste has been reported for a two-stage pyrolysis and partial oxidation process. Co-gasification of biomass with polymer waste has also been shown to increase the amount of hydrogen produced while the CO content reduced. The production of bulk chemicals, such as acetic acid, from polyolefins via oxidation using NO and/or O<sub>2</sub>, is also possible.

#### 3.5.3. Cracking/pyrolysis

Cracking process break down polymer chains into useful lower molecular weight compounds. The products of plastic pyrolysis process could be utilized as fuels or chemicals. Three different cracking processes such as hydrocracking, thermal cracking and catalytic cracking are reported.

**Table 1**  
Calorific values of plastics compared with conventional fuels.

Fuel	Calorific value (MJ/kg)
Methane	53
Gasoline	46
Fuel oil	43
Coal	30
Polyethylene	43
Mixed plastics	30–40
Municipal solid waste	10

**3.5.3.1. Hydrocracking.** Hydrocracking of polymer waste typically involves reaction with hydrogen over a catalyst in a stirred batch autoclave at moderate temperatures and pressures (typically 423–673 K and 3–10 MPa hydrogen). The work reported, mainly focuses on obtaining a high quality gasoline starting from a wide range of feeds. Typical feeds include polyethylene, polyethylene terephthalate, polystyrene, polyvinyl chloride and mixed polymers, polymer waste from municipal solid waste and other sources, co-mixing of polymers with coal, co-mixing of polymers with different refinery oils such as vacuum gas–oil and scrap tyres alone or co-processed with coal. To aid mixing and reaction, solvents such as 1-methyl naphthalene, tetralin and decalin have been used with some success. Several catalysts, classically used in refinery hydrocracking reactions, have been evaluated and include transition metals (e.g., Pt, Ni, Mo, Fe) supported on acid solids (such as alumina, amorphous silica–alumina, zeolites and sulphated zirconia). These catalysts incorporate both cracking and hydrogenation activities and although gasoline product range streams have been obtained, little information on effect of metal and catalyst, surface areas, Si/Al ratio or sensitivity to deactivation is quoted.

**3.5.3.2. Thermal cracking.** Thermal cracking, or Pyrolysis, involves the degradation of the polymeric materials by heating in the absence of oxygen. The process is usually conducted at temperatures between 350 and 900 °C and results in the formation of a carbonized char (solid residues) and a volatile fraction that may be separated into condensable hydrocarbon oil consisting of paraffins, isoparaffins, olefins, naphthenes and aromatics, and a non-condensable high calorific value gas. The proportion of each fraction and their precise composition depends primarily on the nature of the plastic waste but also on process conditions. The extent and the nature of these reactions depend both on the reaction temperature and also on the residence of the products in the reaction zone, an aspect that is primarily affected by the reactor design. However, the thermal degradation of polymers to low molecular weight materials requires high temperatures and has a major drawback in that a very broad product range is obtained. Catalytic pyrolysis provides a means to address these problems.

**3.5.3.3. Catalytic cracking/pyrolysis.** In this method a suitable catalyst is used to carry out the cracking reaction. The presence of catalyst lowers the reaction temperature and time. In addition, catalytic degradation yields a much narrower product distribution of carbon atom number with a peak at lighter hydrocarbons and occurs at considerably lower temperatures. From an economic perspective, reducing the cost even further will make this process an even more attractive option. This option can be optimized by reuse of catalysts and the use of effective catalysts in lesser quantities. This method seem to be the most promising to be developed into a cost-effective commercial polymer recycling process to solve the acute environmental problem of plastic waste disposal.

#### 4. Pyrolysis of plastic waste to liquid fuel—the process

Pyrolysis is generally defined as the controlled burning or heating of a material in the absence of oxygen. In plastics pyrolysis, the macromolecular structures of polymers are broken down into smaller molecules or oligomers and sometimes monomeric units. Further degradation of these subsequent molecules depends on a number of different conditions including (and not limited to) temperature, residence time, and the presence of catalysts and other process conditions. The pyrolysis reaction can be carried out with or without the presence of catalyst. Accordingly, the reaction will be thermal and catalytic pyrolysis. Since majority of plastic

used are polyolefins, so extensive research has been done on this polymer which is summarised as below.

##### 4.1. Thermal pyrolysis of polyolefins

The non-catalytic or thermal pyrolysis of polyolefins is a high energy, endothermic process requiring temperatures of at least 350–500 °C [30–32]. In some studies, temperatures as high as 700–900 °C are essential in achieving decent product yields [33–35]. Thermal pyrolysis of both virgin and waste plastics as well as other hydro-carbonaceous sources has been studied extensively in the past. A good number of these thermal cracking studies are on polyethylene [30,36–50], polystyrene [32,36–40], and polypropylene [31,37,38,41–55]. On the other hand, only a few have worked on the thermal decomposition of other common plastics such as polyvinylchloride [56,57], polymethyl methacrylate [45], polyurethane [58] and polyethylene terephthalate [57].

Generally, thermal cracking results in liquids with low octane value and higher residue contents at moderate temperatures, thus an inefficient process for producing gasoline range fuels [38,52]. The gaseous products obtained by thermal pyrolysis are not suitable for use as fuel products, requiring further refining to be upgraded to useable fuel products [59,60]. A few researchers have sought to improve thermal pyrolysis of waste polyolefins without employing the use of catalysts; however these changes either yielded insignificant improvements or added another level of complexity and costs to the system [52,61].

##### 4.2. Catalytic cracking of polyolefins

Addition of catalyst enhances the conversion and fuel quality. As compared to the purely thermal pyrolysis, the addition of catalyst in polyolefin pyrolysis.

- (1) Significantly lowers pyrolysis temperatures and time. A significant reduction in the degradation temperature and reaction time [62] under catalytic conditions results in an increase in the conversion rates for a wide range of polymers at much lower temperatures than with thermal pyrolysis [63–65].
- (2) Narrows and provides better control over the hydrocarbon products distribution in Low density polyethylene (LDPE) [66,67], High density polyethylene (HDPE), polypropylene [68,69] and polystyrene [70,71] pyrolysis. While thermal pyrolysis, results in a broad range of hydrocarbons ranging from C<sub>5</sub> to C<sub>28</sub> [58], the selectivity of products in the gasoline range (C<sub>5</sub>–C<sub>12</sub>) are much more enhanced by the presence of catalysts [55,64,72]. Again, oils obtained by catalytic pyrolysis contain less olefins and more branched hydrocarbon and aromatic content [62,73].
- (3) Increases the gaseous product yields. Under similar temperatures and reaction times, a much higher gaseous product yield is observed in the presence of a catalyst for polyethylene [64,74].

The dramatic effect of catalyzed decomposition of polymers has spurred a wave of research in the area of catalysis and polymer degradation. And thus, Catalytic degradation of plastics is found to have greatest potential to be developed into a commercialized process [75]. One of the most successful example being the Alka Zadgaonkar's Unique Waste Plastic Management & Research Company plant in India which could produce fuel oil from waste plastics at par with the regular gasoline. The Table 2 gives the comparison of different fuel properties for the fuel produced from waste plastics in Zadgaonkar's process with regular gasoline [76].

From the table, it is clear that the oil produced in this process resembles the regular petrol in all respects and reported to give

**Table 2**

Comparison of waste plastics fuel to regular gasoline.

Properties	Regular gasoline	Plastic waste fuel
Colour, visual	Orange	Pale yellow
Specific gravity at 28 °C	0.7423	0.7254
Specific gravity at 15 °C	0.7528	0.7365
Gross calorific value	11210	11262
Net calorific value	10460	10498
API gravity	56.46	60.65
Sulphur content (by mass)	0.1	<0.002
Flash point (Abel) (°C)	23	22
Pour point (°C)	<−20	<−20
Cloud point (°C)	<−20	<−20
Reactivity with SS	Nil	Nil
Reactivity with MS	Nil	Nil
Reactivity with Cl	Nil	Nil
Reactivity with Al	Nil	Nil
Reactivity with Cu	Nil	Nil

better mileage as compared to commercial petrol. In addition, the cost of production is also reported to be very less [76,151].

#### 4.2.1. The hydrocarbon cracking mechanism

**4.2.1.1. Mechanism of thermal degradation.** As a rule, the plastic pyrolysis follows complex routes that cannot be described by one or more chemical reactions, but still rather imperfectly by either empirical formulas featuring fractional stoichiometric coefficients or compressive systems of elementary reaction, i.e. reaction that really occurs as written [77].

A detail study on the mechanism for the thermal decomposition of polymers is proposed by Cullis and Hirschler [78]. The four different mechanisms proposed are: (1) End-chain scission or unzipping, (2) Random-chain scission/fragmentation, (3) Chain-stripping/elimination of side chain, (4) Cross-linking. The decomposition mode mainly depends on the type of polymer (the molecular structure). The following Table 3 describes the reaction pattern of different thermoplastics where first three types of mechanism is being followed [77]. This has been shown as below [79].



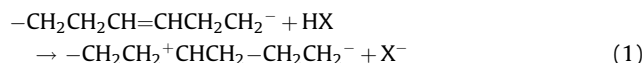
Eqs. (1) and (2) represent the thermal degradation and Eq. (3) represents the random degradation route of the polymers pyrolysis. The fourth type of mechanism i.e. cross linking often occurs in thermosetting plastics upon heating at high temperature in which two adjacent 'stripped' polymer chains can form a bond

resulting in a chain network (a higher MW species). An example is char formation.

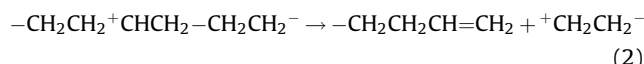
**4.2.1.2. Mechanism of catalytic degradation.** Garforth et al. [79] have investigated catalytic degradation of polyolefins using TGA as a potential method for screening catalysts and have found that the presence of catalyst led to the decrease in the apparent activation energy. Different mechanisms (ionic and free radical) for plastic pyrolysis proposed by different scientists are as given below.

Reaction occur by carbonium ion chemistry includes different steps such as H-transfer, chain/beta-scission, isomerisation, oligomerisation/alkylation, aromatization which is influenced by acid-site strength, density and distribution [80]. Solid acid catalysts, such as zeolites, favor hydrogen transfer reactions due to the presence of many acid sites [79]. The acid strength of solid acids is characterized by both Brønsted and Lewis acid sites; however, the presence of Brønsted acid sites has been observed to support the cracking of olefinic compounds [62]. A study of the Brønsted and Lewis acid sites in polyolefin cracking has been reviewed by several authors [81–84]. Furthermore, in the case of crystalline solid acids, the majority of the acid sites are believed to be located within the pores of the material, such as with zeolites [85]. Thus micro-porosity of porous solid acids is an important feature in assessing the level of polyolefin cracking over such catalysts. The carbonium ion mechanism of catalytic pyrolysis of polyethylene can be described as follows [10].

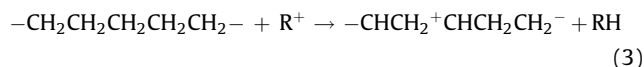
- (1) Initiation: Initiation may occur on some defect sites of the polymer chains. For instance, an olefinic linkage could be converted into an on-chain carbonium ion by proton addition:



The polymer chain may be broken up through  $\beta$ -scission:



Initiation may also take place through random hydride-ion abstraction by low-molecular-weight carbonium ions ( $\text{R}^+$ )



The newly formed on-chain carbonium ion then undergoes  $\beta$ -scission as in Eq. (2).

- (2) Depropagation: The molecular weight of the main polymer chains may be reduced through successive attacks by acidic sites or other carbonium ions and chain cleavage, yielding an oligomer fraction approximately  $\text{C}_{30}\text{--C}_{80}$ ). Further cleavage

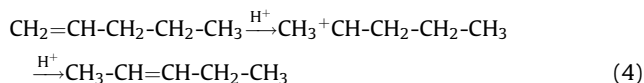
**Table 3**

Mode of thermal decomposition of different thermoplastics and products.

Resin	Mode of thermal decomposition	Low temperature products	High temperature products
Polyethylene	Random chain rupture (involves random fragmentation of polymer along polymer length, results in both monomers and oligomers)	Waxes, paraffin oil, $\alpha$ -olefins	Gases and light oils
Polypropylene	Random chain rupture	Vaseline, olefins	Gases and light oils
Polyvinyl chloride	Chain-stripping (Side chain reactions involving substituents on the polymer chain i.e. elimination of reactive substitutes or side groups (HCl) on the polymer chain, chain dehydrogenation and cyclization)	HCl (<300 °C), Benzene	Toluene (>300 °C)
Polystyrene	Combination of unzipping and chain rupture, forming oligomers	Styrene and its oligomers	Styrene and its oligomers
Polymethyl methacralate	Unzipping (Cracking is targeted at chain ends first, and then successively proceeds down the polymeric length, results in monomer formation)	Monomer Methyl methacralate	Less Methyl methacralate, More decomposition
Polytetrafluoro ethylene	Unzipping	Monomer tetrafluoro ethylene	
Polyethylene terephthalate	$\beta$ -Hydrogen transfer, rearrangement and decarboxylation	Benzoic acid and vinyl terephthalate	
Polyamide 6	Unzipping	Caprolactum	

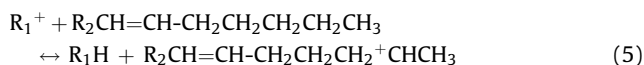
of the oligomer fraction probably by direct  $\beta$ -scission of chain-end carbonium ions leads to gas formation on the one hand, and a liquid fraction (approximately  $C_{10}$ – $C_{25}$ ) on the other.

- (3) Isomerization: The carbonium ion intermediates can undergo rearrangement by hydrogen- or carbon-atom shifts leading to a double-bond isomerization of an olefin:



Other important isomerization reactions are methyl-group shift and isomerization of saturated hydrocarbons.

- (4) Aromatization: Some carbonium ion intermediates can undergo cyclization reactions. An example is when hydride-ion abstraction first takes place on an olefin at a position several carbons removed from the double bond, the result being the formation of an olefinic carbonium ion:



The carbonium ion could undergo intramolecular attack on the double bond:

Such reactions provide a route to cyclization and formation of aromatics.

Sekine and Fujimoto [86] have proposed a free radical mechanism for the catalytic degradation of PP using Fe/activated carbon catalyst. During degradation, methyl, primary and secondary alkyl radicals are formed, and by hydrogen abstractions and recombination of radical units, methane, olefins and monomers are produced [47]. The various steps in catalytic degradation are shown below. In initiation step, random breakage of the C–C bond of the main chain occurs with heat to produce hydrocarbon radicals. In propagation, the hydrocarbon radical decomposes to produce lower hydrocarbons such as propylene, followed by  $\beta$ -scission and abstraction of H radicals from other hydrocarbons to produce a new hydrocarbon radical. Disproportionation or recombination of two radicals is termination reaction. During catalytic degradation with Fe/activated charcoal in a  $\text{H}_2$  atmosphere, hydrogenation of hydrocarbon radical (olefin) and the abstraction of the H radical from hydrocarbon or hydrocarbon radical generate radicals, enhancing degradation rate. In a reaction temperature lower than  $400^\circ\text{C}$  or a reaction time shorter than 1.0 h, many macromolecular hydrocarbon radicals exist in the reactor, and recombination occurs readily because these radicals cannot move fast. However, with Fe/Activated Carbon in a  $\text{H}_2$  atmosphere, these radicals are hydrogenated and therefore recombination may be suppressed. Consequently, it seems as if the decomposition of the solid product is promoted, including low polymers whose molecular diameter is larger than the pore size of the catalysts.

*Initiation:*



*Chain reaction:*



*Termination:*

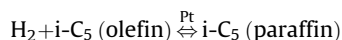
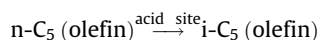
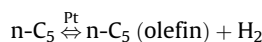


*In presence of Fe/Activated Carbon +  $\text{H}_2$ :*



Wall et al. [87] have studied the catalytic degradation of waste plastics and have found that when these polymers have been heated above  $380^\circ\text{C}$ , they undergo depolymerisation and degradation by a free radical chain reaction.

Plastic degradation in presence of a reforming catalyst is explained differently. The reforming catalysts are said to be bifunctional, in view of the two kinds of active sites playing different roles. The metallic sites catalyze hydrogenation and dehydrogenation reactions, while the acidic sites on the support catalyze isomerization reactions. A proper combination of these two functions can promote a variety of reforming reactions such as isomerization where straight-chain paraffins are isomerized to branched-chain molecules, dehydrocyclization where straight-chain paraffins are converted to cycloparaffins, and dehydrogenation in which naphthenes are dehydrogenated to aromatics; the octane numbers of gasoline-range hydrocarbons are improved without changing their carbon numbers. The most commonly used reforming catalyst is  $\text{Pt}/\text{SiO}_2\text{--Al}_2\text{O}_3$  with about 0.5 wt% Pt only. The following overall reaction scheme for n-pentane isomerization illustrates the reforming reactions [10].



#### 4.3. Process design

Many have demonstrated that plastics waste can indeed be converted to useful chemical feedstock by both non-catalytic and catalytic pyrolysis. Literature shows that the distribution can also be affected by different process parameters such as feed composition (plastic type), catalyst loading, size of the catalyst, the means of polymer and catalyst contact during degradation, reactor type, and degradation process conditions such as temperature, pressure, residence time. The effect of various process variables are described below.

##### 4.3.1. Effect of feed composition (type of polymer) on product yield and distribution

The primary pyrolysis products relates directly to the chemical structure and decomposition of the resin, and also to the mechanism of its decomposition (Purely thermal or catalytic). In general, the decomposition of polyolefin mixtures occurs roughly in the same range as their virgin counterparts ( $350$ – $500^\circ\text{C}$ ). However, waste polyolefins may degrade at slightly lower temperatures and achieve higher conversions than the respective virgin polyolefins [63,88–92]. As with virgin plastics, the addition of catalysts in waste pyrolysis greatly influence product yields and conversion rates; however, the disparities between waste and virgin polyolefin pyrolysis lie mainly in the resulting product compositions [8,71,93–95]. It is clear that during pyrolysis, interactions between the different materials in a waste feed have a significant effect on the selectivity of specific liquid and gaseous product components [96].

Pyrolysis of plastics yields liquid, gas and solid residue products. Liquid product yields greater than 82.5% and as high as 96% have been found for polyethylene and polypropylene



pyrolysis [49,58]; however, these are obtained at high temperatures and within a reaction time of approximately one hour. Polyethylene and polypropylene decomposes in to a range of paraffin and olefins and the paraffin to olefin ratio decreases with increase temperature and time [77]. PONA distributions of FCC catalyzed decompositions show that the olefin yield far exceeds the yield of paraffins, naphthenes, or aromatics (PNAs) in the pyrolysis of polypropylene and HDPE [96,98,99]. Lee et al. [99,100] also showed that the catalytic degradation of waste LDPE produced more paraffins and aromatics than those of waste HDPE and polypropylene.

The pyrolysis of polyethylene and polypropylene is characterized by low monomer yield [56,94], where as polystyrene mostly gives monomeric units as the main product. Polystyrene pyrolysis exhibits high yields of aromatics, as high as 97 wt% of liquid product [45,99,101,103]. This is attributed to the polycyclic nature of polystyrene and the thermodynamic challenge posed in converting cyclic compounds to aliphatic chains or alkene compounds [101]. A closer look at the aromatic yield in many of these catalyzed reactions reveals that, the product selectivity is higher for benzene, toluene and ethyl benzene unlike in thermal pyrolysis, where the main product is styrene [33,45,101–103]. Again, the results obtained in the thermal depolymerisation of polymethylmethacrylate are noteworthy since at 723 K, a 98% yield to the monomer has been reported [19].

Mixture of polyethylene and polystyrene decomposes as usual in the case of polystyrene, with the pyrolysis yield somewhat more saturated, the polyethylene providing the required hydrogen. The decomposition of the polyethylene is somewhat accelerated by the presence of polystyrene [77]. This has been explained due to the radicals formed during polystyrene decomposition. The conversions of polyethylene and polypropylene are improved by polystyrene addition [71,92,103]. Conversely, polystyrene decomposition seems to be immune to effects by either of the other polyolefins. Typically, polyethylene pyrolysis favors mostly the formation of paraffins; however, upon increasing its polystyrene or polypropylene content, the yield of aromatic and alkenic products is greatly enhanced, thus improving its octane value [95,104]. This clearly indicates the similarity and variance in the cracking mechanisms in different polyolefins.

#### 4.3.2. Effect of catalyst loading

The use of catalyst in pyrolysis of plastics influences upon kinetics and mechanism, and hence, the product distribution. Conversion increases with catalyst loading [105–107]. The most commonly researched solid acid catalysts in plastic waste pyrolysis include molecular sieves, such as silica alumina [38,75,108,109], zeolites [110–113], and MCM-41 [114–116]. Amongst the numerous kinds of zeolites investigated in polyolefin pyrolysis, Beta [117], USY [118], ZSM-11 [116], REY [59,119], Mordenite [113,120], ZSM-5 [121,122] are the most commonly used. Reports on the FCC process are also found in literature [123–125]. Other catalytic materials such as clays (montmorillonite, saponite) [126], reforming catalysts, activated carbon, metal oxides, metal complexes of the type  $MCl_n-AlCl_3$  or  $M(AlCl_4)_n$  ( $M = Li, Na, K, Mg, Ca, Ba; n = 1-2$ ), and alkali metal carbonates or alkaline metal carbonates have also been tested for polymer degradation [10]. The common features shared by the different zeolite catalysts are proper acid strength, pore size and pore structure. Generally, the level of the catalyst activity in polyolefin pyrolysis increases with increasing number of acid sites [62]. Thus, zeolite based catalysts achieve higher conversion than non-zeolitic catalysts [73,75,93]. The effect of some specific zeolitic and other catalysts used by the different researchers for plastic pyrolysis is as summarised below.

The product distribution of the catalytic degradation of high-density polyethylene on different zeolites yields hydrocarbons

from  $C_3$  to  $C_{15}$ . The structure of the zeolitic framework has shown a significant influence on the product distribution. Alkanes are the major products with US-Y, Y, and  $\beta$ -zeolites, whereas alkenes are the major products with mordenite and ZSM-5. The majority of alkanes are reported to be isoparaffins, having a high octane number; this speaks for an increased fuel quality. A small amount of cycloproducts and aromatics are formed on all samples. This is an important advantage of the catalytic degradation, as environmental concern about aromatics grows and strict legislation for low levels of aromatics in fuels is under discussion [112].

Songip et al. studied the conversion of polyethylene to transportation fuel using REY (Rare earth Y) catalyst (7.8 Å pore size and 11.8 Å supercage) in addition to other acid and non-acid catalysts. REY is reported to be best for oil conversion, gasoline yield, and research octane number of gasoline. It is concluded that the performance of REY zeolite is attributable to its stability, adequate acidity, and relatively large pores into which oil molecules are allowed to penetrate [127].

The catalytic degradation of high-density polyethylene on ultrastable-Y zeolite has significantly reduced the degradation temperature compared with pure thermal degradation in the absence of a catalyst. The products of the catalytic degradation were hydrocarbons in the gasoline range ( $C_3$ – $C_{15}$ ) were the heaviest detected product. The majority of the products are isoparaffins, suggesting high octane number, speaks for a high-quality fuel as a product of a catalytic degradation process [97].

Clinoptilolite zeolites (with pore structure of a monoclinic framework consisting of a 10-membered ring (7.6 Å × 3.0 Å) and an 8-membered ring (3.3 Å × 4.6 Å), and is a silica-rich member of the heulandite family either proton-exchanged or further treated by hydrochloric acid are efficient catalysts for the conversion of polypropylene to gasoline-range liquid chemicals. In the degradation of polypropylene, the acidic sites of medium acid strength seem necessary for the formation of carbenium ion and cracking of carbon chains. Pore volume is another important character for the further cracking of initially degraded fragments. High degradation temperature offered lighter hydrocarbons by accelerating the cracking reactions. When it is dealuminated by the HCl treatment, the gaseous products (mainly ethane, propane, propylene and butene) increased greatly. Even though the dealuminated catalysts possess lower acid amount, they have relatively larger pore size, therefore, the degraded liquid components over these catalysts will have more chance to stay in the pore for further cracking to lighter gaseous products. Thermal degradation on clinoptilolite showed high amount of residues, but the proton exchanged clinoptilolite showed practically no formation of residue [128].

Pyrolysis of polyethylene using ZSM-5 yields greater percentage of gaseous products than oil. This extraordinary yield is explained due to a strongly acidic property and a unique larger intracrystalline pore channel structure of ZSM-5 which helps in excellent catalytic efficiency on cracking, isomerization and aromatization. The larger intracrystalline pore channel structure allows more cracking of the heavy petroleum chemicals. In addition, ZSM-5 possesses a smaller pore diameter (5.4–5.6 Å) among zeolites. Since the initially degraded materials on the external surface of catalyst can be dispersed into the smaller internal cavities of catalyst, they can be further degraded to the smaller size of gaseous hydrocarbons, leading to the remarkably high yield production of gaseous material. Grieken et al. [129] using batch type reactors also reported that ZSM-5 accelerated the degradation of plastics, especially polyethylene, giving a large production of gaseous materials and a low oil yield. Similarly, HZSM-5 also reportedly yields more gas fraction and aromatic hydrocarbons in the catalytic degradation of polyethylene. Also this catalyst increases the ratio of branched hydrocarbon to normal hydrocarbon and decreases the formation of straight chain

paraffins and olefins. Sharratt et al. [130] reported that the gaseous material rich in  $C_3$ – $C_5$  olefins is obtained in high yield from the catalytic degradation of high-density polyethylene (HDPE) over HZSM-5 in a fluidized bed reactor. All zeolites increased olefin content in oil product, particularly ZSM-5 and zeolite-Y enhanced the formation of both aromatics and branched hydrocarbons simultaneously. ZSM-5 showed the greatest catalytic activity on cracking of heavy hydrocarbons to small gaseous hydrocarbons and formation of aromatics [121,122].

The use of nanocrystalline HZSM-5 allows greater yields of gas fractions at mild temperatures and a higher selectivity to the products obtained than those achieved by thermal cracking. First, polyethylene is cracked over the acid sites on the external surface of the zeolite; a part of the compounds produced can then diffuse into the internal active surface through the zig-zag pores and overcrack giving lighter compounds. Due to the size restriction of the pores, gases are produced mainly in the pores while waxes are the result of external cracking. The temperature affects the gas and wax yields. Gas production increases as the temperature rises. However, when the temperature exceeds 500 °C, some HDPE is cracked thermally, increasing the wax yield and varying the wax and gas compositions. If the catalytic pyrolysis temperature is too low (350–400 °C), the polymer is not fully cracked and a solid residue is produced in the reaction bed. The gases are mainly composed of olefins. Cracking reactions ( $\beta$ -scission) control the reaction mechanism inside the pores. Due to their small dimensions, HZSM-5 pores inhibit bimolecular reactions, which are a source for paraffin production. Terminal olefins are not produced in significant quantities because of the strong effect of isomerization reactions [122].

Mordenite is reported to enhance the rate of pyrolysis reaction, but it produce much greater fraction of  $C_{11}$ – $C_{13}$  paraffins and greatest amount of coke explained due to its bottleneck crystalline structure [121].

With silica-alumina (SA), all of the polyethylene is found to be converted to liquid products with high yields (77–83 wt%) and without any wax production. The liquid products were distributed in the range of  $n$ - $C_5$ , to  $n$ - $C_{20}$  and mostly  $C_5$ – $C_{15}$  [131]. Silica-alumina also reported to increase the olefin content in oil product [121]. The effects of silica-alumina SA-1 (have  $SiO_2/Al_2O_3$  ratios of 83.3/16.7) and silica-alumina SA-2 (have  $SiO_2/Al_2O_3$  ratios 21.1/78.9) catalysts with different  $SiO_2/Al_2O_3$  ratio is studied by Md Azhar et al. [131] in order to investigate the effects of acidity of silica-alumina on liquid product composition. The yield of liquid products was 68 wt% for SA-1 compared to 77 wt% for SA-2. With SA-1, liquid products were distributed in the range of equivalent carbon numbers of  $n$ - $C_5$  to  $n$ - $C_{15}$  (boiling point range 36–216 °C), very similar to those of commercial gasoline. Therefore, the SA-1 catalyst degraded the polyethylene sample into much lighter hydrocarbon fuel oil than the SA-2 catalyst. So it can be concluded that the yield and composition of the liquid products can be controlled by altering the  $SiO_2/Al_2O_3$  ratio i.e. the acidity of the catalyst. As the  $SiO_2/Al_2O_3$  ratio of the SA-1 and SA-2 catalysts is different, both the acid strength and acid content of these catalysts may differ. Amorphous silica-alumina also shows a great activity on cracking polyethylene and polypropylene to lighter hydrocarbons. Since amorphous silica-alumina appears to have a higher fraction of total acidity in the strong acid range, it might tend to favor tight binding of carbenium ions to the surface and to carry out continuous cracking. It generated a pronouncedly high yield of lighter olefins due to strong acidity, but was far inferior to zeolites in the formation of aromatics and branched hydrocarbons because of amorphous structure [121].

Mesoporous silica (FSM) with no acid sites is found to have faster rate of polymer degradation than that of non-catalytic thermal degradation and comparable to that over solid acid

catalysts. This result is attributed due to the fact that mesoporous silica FSM, having arrays of uniform hexagonal pores of 2.7 nm accelerates the degradation of polymers, even though the FSM catalyst does not contain any significant acid sites. Again, when compared with non-catalytic thermal degradation, FSM not only accelerates the rate of degradation of polymers but also degrades the heavier waxy compounds into lighter liquid hydrocarbons [132].

Studies employing mesoporous aluminosilicate such as MCM-41 (Mobile Crystalline Material) suggest that it increases the product character and also reduces the reaction temperature [109]. HMCM-41 also leads to a high conversion of the plastic mixture because of its large pore size, which promotes the access of the polymer molecules to the acid sites [133]. Catalytic reforming over Al-MCM-41 generated a lower proportion of gaseous hydrocarbons and a higher yield of gasoline type condensable products, which was attributed to its weaker acid properties and larger pore dimensions. Catalytic conversion over this meso structured material showed a lower selectivity towards the formation of aromatic products but yield higher proportions of liquid iso-paraffins and olefins. The composition of this oil fraction is comparable to commercial gasoline fuel [134].

Two smectites such as saponite and a montmorillonite, as well as their Al-pillared derivatives, are tested for their performance in the catalytic cracking of polyethylene. Below about 600 K, those catalysts proved to be less active than zeolites. However, this picture is drastically changed with temperature, as the clay catalysts were able to completely decompose polyethylene after a small increase in the process temperature. Moreover, they proved superior to zeolites with respect to the formation of liquid hydrocarbon fuel. The yield to liquid products was around 70%. This higher liquid yield of clay-based catalysts is attributed to their weaker acidity, which does not sustain over cracking to small molecules and is also reflected in the liquid product distribution. Clay catalysts furnish hydrocarbon liquid products that are considerably heavier than those from zeolite catalysts. In addition, the clay catalysts furnish products that, in the overwhelming majority, are in the gasoline range. Furthermore, the predominance of alkenes as products over the clay catalysts is due to the significantly lower occurrence of hydrogen-transfer secondary reactions because of the milder acidity of clays. This differentiation probably also explains the lower coke formation over the clay-based catalysts [126].

FCC (Fluid catalytic cracking) catalysts usually have faujasite structure with a ratio of Si/Al greater than 1.5. It is formed by the arrangement of truncated octahedra forming cages of 13 Å diameter, and the pore opening to these cages are 12-membered rings approximately 7.4 Å. The equilibrium FCC catalyst had good catalytic activity for producing light hydrocarbon liquids with carbon number  $C_6$ – $C_{15}$ . It is stated that  $C_2$  and  $C_4$  fractions are dominating mainly in gases on the cracking of polyethylene [135].

Activated carbon catalyzed plastics cracking yield normal alkanes and the amount of isoalkanes is very small. When Pt impregnated on activated carbon was tested, the aromatic yield is reported to reach as high as 50% of the plastic sample; it was suggested that this is due to a good combination of cracking and dehydrocyclization activities of the catalyst [11].

Synthesized fly ash catalyst (SFC) is found to decrease the decomposition temperature and the initiation time for pyrolysis and is more effective than some zeolite catalysts or no catalyst. For the pyrolysis of polyethylene, but the pyrolysis oil produced by SFC appeared to be creamy phase and is not in the full boiling point range of diesel. In case of paralyzing polypropylene by SFC, better oil is made for the alternative fuel oil which can be used without problem as commercial diesel oil [136].

The lead sulfide catalytic pyrolysis enables polyethylene to be converted into liquid, gas and wax with nearly 100% efficiency. As the char formation with lead sulfide is negligible therefore the catalyst can be used several times without treatment. No side products are associated with the method. The pyrolysis products mainly consisted of paraffinic and olefinic compounds. Distillation data and other physicochemical tests for fuel oil show that, these oils are suitable to be used as fuel oil for different energy purposes [137].

Catalysts such as metal oxides, metal complexes, and alkali metal carbonates or alkaline metal carbonates have appeared to be used mainly for enhancement of monomer recovery [10]. Degradation of polyethylene on solid bases (ZnO, MgO, TiO<sub>2</sub>) yield more oils than on solid acids, though the time required to complete the degradation on solid bases is much longer than on solid acids. The composition of oil on solid bases is reported to be rich in 1-olefins and is poor in aromatics and branched isomers. So, that oils mainly consisting of olefins are not expected for fuel oils because of their polymerization during preservation and/or transportation. Moreover, a low octane number is expected for the oils produced on solid bases, since the oils mainly consisted of straight chain hydrocarbons; n-paraffins and 1-olefins. Similarly, more amount of styrene was yielded from waste polystyrene degraded on solid bases rather than on solid acids. Productions of benzene and indan are one of the features of the polystyrene degradation on solid acids. The solid bases such as BaO and K<sub>2</sub>O yields more than 80 wt% both styrene monomer and dimer. Again, thermal degradation of polystyrene films dispersing BaO powders produce around 90 wt% of both styrene monomer and dimer at 623 K. These styrene monomer and dimer could be reused for the production of polystyrene. In this sense, the polystyrene films dispersing BaO catalyst can be considered as one of the models of the recyclable polymer, which has been extensively studied from the view point of the technology for saving carbon resources as well as for environmental issues [138].

#### 4.3.3. Effect of catalyst contact mode

One may investigate the catalytic steps involved in polymer degradation by considering different modes of catalyst introduction to the polymer feed. Sakata et al. [75] investigated two modes of contact in the batch pyrolysis of polypropylene using various solid acids: “liquid phase contact” and “vapor phase contact”. For the catalytic degradation in the liquid phase contact, both catalyst and polymer are placed in the reactor and heated to the operating temperature. Whereas, with the vapor phase contact mode, the polymer is first thermally degraded into hydrocarbon vapors and then contacted with the catalyst. It has been observed that liquid phase pyrolysis retards the escape of evolving products, thus enhancing interactions and hydrocarbon vapors undergo further cracking in the vapor phase whereas the product yield in the liquid or melt phase contact is reported not to be differ significantly from that obtained by purely thermal degradation of polypropylene [77].

#### 4.3.4. Effect of particle/crystallite size of catalyst on product distribution

The effect of catalyst particle size has only been sparsely studied in literature. You et al. [139] investigated the effect of particle size of zeolites on the catalytic degradation of polyethylene wax and found that whereas conversion decreased with particle size, product quality increased. Furthermore, particle sizes in the nano-range have been investigated. Serrano et al. [140] reported conversions as high as 90%, temperatures less than 350 °C for the cracking of polypropylene, LDPE and HDPE using nano-crystalline ZSM-5. Aguado et al. [105] observed similar results in the batch pyrolysis of polypropylene and LDPE mixtures using

nano-HZSM-5. Based on these results, it can also be deduced that nano-ZSM-5 catalyzed reactions result in very high gas yields in the range of C<sub>3</sub>–C<sub>6</sub> products, and apparently in much higher concentrations than is observed with micron-sized ZSM-5. These nano-sized particles are so effective because of their increased surface area. Conversely, high surface area combined with a very small pore system poses great difficulty in achieving decent amounts of gasoline range products in the C<sub>5</sub>–C<sub>12</sub> range. So, the nano-catalyst selectivity to liquid products is also very limited [120,140]. This could be resolved by investigating the particle size effect with catalysts that are selective to gasoline range liquid products such as FCC catalysts.

#### 4.3.5. Effect of reactor type

The type of reactor used determines mainly the quality of heat transfer, mixing, gas and liquid phase residence times, and the escape of primary products. A wide range of reactors have been used on a lab-scale in polyolefin pyrolysis. The reactor set-ups investigated so far fall under one of the following categories: Batch reactor, semi-batch reactor, Continuous flow reactor (CFR), modifications or combinations of either of these.

A common variable in batch and semi-batch operations is nitrogen which is used for the continuous removal of volatiles from the reactor vessel. The products are then collected by passing the vapors through a condensation system. Most are made out of Pyrex or stainless steel. A key disadvantage with this is the high reaction times observed. Furthermore, under batch operation, it seems that the potential of a catalyst is minimized with similar product yields to thermal at similar conditions. From an industrial viewpoint, continuous reaction systems are preferred to batch set-ups for operational reasons [62,64].

In fixed bed semi-batch reactor, polymer and catalysts samples are heated separately and reacted by vapor phase contact. Degraded polymer fragments are carried to the catalyst bed/mesh by a carrier gas, in most cases N<sub>2</sub>. Typically the catalyst bed is heated to a higher temperature than the polymer bed [64,141].

More recently, researchers have moved focus towards reactors with greater feasibility in the industrial arena such as fluidized bed reactors. Riser simulator reactors are fluidized batch reactors, specifically designed to simulate similar conditions found in a catalytic riser reactor used in the FCC process. It is adapted for liquid phase catalytic reaction, in which heat from the catalysts could vaporize the melt polymer feed while simultaneously cracking the resulting hydrocarbons [142–144]. The University of Hamburg, in particular, has done a lot of research in feedstock recycling from waste plastics using FCCs, and has subsequently developed the ‘Hamburg process’ which makes use of an indirectly heated fluidized bed [60,101]. During catalytic cracking, quartz sand is replaced by the respective FCC catalyst as packing material. Amongst the various catalysts investigated, FCCs produced the most decent liquid yields in polyethylene pyrolysis.

Unlike a batch reactor, a fluidized bed reactor is suited for pyrolysis because it provides very good heat and material transfer rates hence generating largely uniform products. However, the disadvantages are many and include: broad residence time distribution of solids due to intense mixing, attrition of bed internals and catalyst particles, difficulty in scale-up, defluidization problems, requires large amounts of catalysts, low liquid yields due to ‘over cracking’.

On the other hand, other continuous systems, such as the three-step continuous flow pyrolysis process involving a pre-heat, cracking reactor and separation zones, have been investigated by a few [8,49,61,66]. In this method the polymer is first pre-heated to a molten state in a CFR such as an extruder and driven into the ‘reactor’ where it is further ‘cracked’ at elevated temperatures.

#### 4.3.6. Effect of other process parameters

The effect of other process parameters such as reaction temperature, pressure, reaction time and catalyst loading has been investigated. These are summarized in Table 4.

### 5. Economic and ecological aspects of catalytic pyrolysis of plastics

The new technologies and economics have come to play an important role in plastics recycling. As described in previous section, plastic recycling principally refers to recovery, which is divided into material recycling and energy recovery. Material recycling is again divided into mechanical and feedstock recycling. The choice between these methods will depend on the types of plastics waste, the relative ease/difficulty in total or partial segregation from other plastics and/or other waste materials, ecological and cost aspect involved in the process. While determining economic boundary conditions of plastics recycling, it is necessary to make a distinction between: (i) mechanical recycling to the same or similar applications, (ii) mechanical recycling to new areas of applications, (iii) incineration and energy recovery, cement kilns, incineration for power generation, (iv) feedstock recycling to form different products like conversion to monomer, fuel, reducing agent in blast furnace for the production of iron, gasification and liquefaction.

Worldwide, mechanical recycling is the most preferred and accepted method of plastics recycling. However, it includes a wide variety of processing techniques and a broad range of processing methods requires lot of energy, which increase the cost depending on the degree of contamination. After collection of the portions that can be recycled by mechanical recycling, there remain numerous very small, heavily contaminated articles or cross-linked products or products contaminated with hazardous substances. Heavily contaminated plastics waste collected from domestic waste stream can be utilized by energy recovery from waste incineration plants. Cost of this system of recovery is considered highest among all the alternatives. Again, incinerator design and operation depends upon the type of waste to be incinerated and another important factor to carry out this process is to minimize the harmful emissions. Non-adherence to these two basic principles caused serious failures of various incineration activities in the 1980s raising doubt about the effectiveness of this process itself. Feedstock recycling would be a better alternative from cost and ecological aspects. As the cost of feedstock recycling

even in the best case of large-scale plants may be similar (as high as) to the cost for incineration and energy recovery and does not produce harmful emission if designed properly. Again this process is complementary to mechanical recycling since it is less sensitive to unsorted or uncontaminated plastic waste and enlarges the overall recycling capacities for large waste quantities to be supplies in future. This is also important today from the global warming point of view and the operator in a developing country is able to cash on the carbon credit as there is reduction in dependence on fossil fuels [148].

Extensive research has been carried out on catalytic pyrolysis of plastics using different catalysts and the process has also been materialized in different countries.

In the early 1990s BP Chemicals, first tested technology for feedstock recycling, using a fluid bed cracking process. Research on a laboratory scale was followed (1994) by demonstration at a continuous pilot plant scale (nominal 50 kg/h) at BP's Grange-mouth site, using mixed waste packaging plastics. The technology was further developed with some support from a Consortium of European companies (Elf Atochem, EniChem, DSM, CREED) and from APME. In 1998, BP Chemicals, VALPAK and Shanks & McEwan, set up a joint project (POLSCO), to study the feasibility of a 25,000 tonnes/y plant, including logistics infrastructure for supplying mixed plastics from Scotland. The process involves initial cleaning of waste plastics to remove the non-plastic impurities and heating them in a fluidised bed reactor operating as 500 °C, in absence of oxygen. Lime absorber is used to remove the HCl produced due to the presence of polyvinyl chloride. The different type plastic that has been used includes polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate and styrenic polymers. The hydrocarbon products (85% yield) can be fed directly to petrochemical plants or to gasoline without further purification [77].

Veba oil developed a commercial process, operating in a temperature range of 350–450 °C and requiring a high hydrogen partial pressure (50–100 bar) using a liquid phase reactor. The technology was realized in the coal-to-oil plant at Bottrop, with a capacity of 40,000 tonnes annually doubled at the end of 1995 [77].

A large pilot plant, with a substantial capacity of 15,000 tonnes/y, was started up in Ludwigshafen in 1994 by the BASF in which plastic waste is converted into petrochemical products using a tubular cracker reactor [77].

A plant operating according to the Hamburg University pyrolysis process was built at Ebenhausen, Germany with a

**Table 4**  
Effect of different process parameters like pyrolysis temperature and heating rate, operating pressure, residence time, presence of gases, such as N<sub>2</sub>, Ar, O<sub>2</sub> or H<sub>2</sub> on pyrolysis.

Process parameter	Results
Pyrolysis temperature and heating rate	Higher operating temperature and high heating rates both enhance bond breaking and favour the production of small molecules [77] Conversion increases with increase of temperature resulting in decrease of aliphatic content. Dermibas et al. [33] observed that gaseous products (C <sub>2</sub> –C <sub>4</sub> ) increases and liquid products (C <sub>5</sub> –C <sub>9</sub> ) decreases with increase in temperature Effect of the catalysts on the yields and structure of products becomes less significant with increasing temperature [91,145]
Operating pressure	Low pressure reduces the condensation of reactive fragments forming coke and heavies [77] Murata et al. [30] demonstrates the inverse relation of pressure to temperature in the pyrolysis of polyethylene. With the higher pressure, the carbon number distribution of gaseous and liquid products, and the molecular weight distribution of reactor contents shifted to the lower molecular weight side
Residence time [34,106,110,146,147]	Key parameter in fluidized bed reactors. Generally conversion increases with residence time  Longer residence time favour a secondary conversion of primary products, yielding more coke, tar, as well as thermally stable products, thus gradually obscuring the effect of original polymer structure [77] Miskolczi et al. [145] observed that the catalyst activity of HZSM-5 and an FCC catalyst decreased with increasing cracking time in the pyrolysis of HDPE waste Effect of residence time on product yield is more pronounced at lower than higher temperatures
Presence of gases, such as N <sub>2</sub> , Ar, O <sub>2</sub> or H <sub>2</sub> [77]	Such presence internally generates heat, dilutes the products and influences upon equilibrium, kinetics, and mechanism



capacity of 5000 tonnes/y. This process was developed by W. Kiminsky in 1883 in which pyrolysis is carried out in an externally heated fluidised bed reactor containing sand [77].

The first report of turning plastic wastes into oil came in 2001 from the People's Daily, China's English language newspaper. An oil refinery in Hunan province had succeeded in processing 30,000 tonnes of plastic wastes into 20,000 tonnes of gasoline and diesel oil that satisfied the provincial standards. Wang Xu, who built the refinery in 1999, started experimenting with waste plastic processing in the 1980s, and later teamed up with Hunan University doctoral tutor Zeng Guangming who gave him scientific advice on decomposing plastic wastes. In the 1980s, Illinois microbiologist Paul Baskis in the United States modified the process to produce a lighter, cleaner oil, but failed to convince investors until 1996, when a company called Changing World Technologies began development with Baskis to make the process commercially viable [149]. Again, the plants with a capacity of 1000 tonnes/annum have been running nearby many cities in China [150].

Environmental Technology Systems Ltd is a U.K. company, incorporated in 2003, which now has the rights to acquire a proven Chinese technology to convert waste plastics into gasoline and diesel fuels produce 2000 tonnes/annum of fuel oil (roughly, half petrol and half diesel) from 2740 tonnes of waste plastics. The balance is 410 tonnes of combustible gas which is used to provide heat for the process. The sole by-product is 330 tonnes of 'slag'. The process is continuous and can handle all plastics including polyvinyl chloride and no pre-sorting is required. The plastic is shredded prior to being passed into the feed-hopper and the process uses non-pressurised modular catalytic reactor running at moderate temperatures of 350–400 °C [151] converts plastic feed into 73% fuel oil, 15% gas and 12% inert ash residue (mainly dirt introduced with the waste). The fuel oil can be burned immediately to produce heat or electricity or it can be fractionated into roughly equal parts transport grade diesel and high-octane gasoline that is lead and sulphur-free. The Technology is "clean". There is no odour. There are no gaseous emissions or liquid effluents beyond modern petrochemicals practice. The eco friendly processing plants produce high quality fuels, which meet or exceed current industry standards for transport grade fuels [152].

In India, a zero-pollution industrial process to convert non-biodegradable and mostly non-recyclable plastic waste into liquid hydrocarbons has been set up at Butibori industrial estate, Nagpur in 2005 by Prof. Alka Zadgaonkar. The Zadgaonkar's Unique Waste Plastic Management & Research Company plant devours a whole range of plastic waste from discarded carry bags to mineral water bottles and broken buckets to polyvinyl chloride pipes, polyethylene terephthalate bottles, even acrylonitrile butadiene styrene plastic material used in the making of computer monitors and TV sets, keyboards, etc. and converts it 100% into liquid hydrocarbon fuels (85%) and gases (15%). This is the World's first continuous process for plastic recycling to liquid fuel [153,154].

Enviro-Hub the waste management and recycling firm announced the construction of Singapore's first US\$ 50 million plastic-to-fuel plant which converts waste plastic into useable fuels and gases. It is building the world's first large-scale, commercial plastic-to-fuel plant. This process is based on patented technology imported from India, for which Enviro-Hub now holds an exclusive license, heats waste plastic with a special catalyst that breaks it down into 85% diesel, 10% liquid petroleum gas and 5% coke [155].

Most recently the projects operating at a full scale includes liquefaction units using continuous stirred tank reactors, at Niigata and Sapporo, Mikasa works, Coke oven pyrolysis by Nippon Steel Corp, high-pressure gasification by EBARA-UBE, ASR gasification at Aomori (Ebara Co.), Glycolysis of polyethylene terephthalate bottles by Teijin [77].

Dumfries Plastics Recycling (DPR), a subsidiary of British Polythene Industries, is a SEPA (Scottish Environment Protection Act) accredited recycling plant. DPR can recycle 5000 tonnes/annum of post-use agricultural stretch film, the only unit in the world capable of doing so. The DPR Washing Plant can also recycle other post-use polyethylene films and is designed to handle heavily contaminated films (some films contain over 50% sand/soil/water) [156].

## 6. Future works

Literature reveals that a number of research efforts on the catalytic pyrolysis of plastics in different conditions using different catalysts and the process have been initiated. However, there are many subsequent problems to be solved in the near future. The present issues are the necessary scale up, minimization of waste handling costs and production cost and optimization of gasoline range products for a wide range of plastic mixtures or waste. The further tasks are

- (1) To constitute the standards for process and products of post-consumer recycled plastics and to adopt the more advanced pyrolysis technologies for waste plastics, referring to the observations of research and development in this field. The pyrolysis reactor must be designed to suit the mixed waste plastics and small-scaled and middle-scaled production.
- (2) The scientist should pay more attention to exploring the recycling and pyrolysis of waste polyvinyl chloride and the optimization of operational conditions of pyrolysis for waste plastics to abate the generation of toxic substances like dioxins and PCBs.
- (3) A novel and more efficient catalyst ought to be studied for the process of pyrolysis which would be cheaper, obtainable on commercial scale and should be regenerated back.
- (4) Process integration through pinch analysis would help reducing the capital investment and also the operating cost and thus would enhance the economic viability of the process.
- (5) A more sophisticated mechanism of catalytic pyrolysis should be explored to improve the process further.

## 7. Conclusion

According to the current statistics, there is continuous rise of consumption and thus cost of petroleum oil, although there has been a temporary drop in demand growth due to the international financial crisis. International Energy Outlook 2008 reports the world consumption of petroleum oil as 84 million barrels per day and that of natural gas as 19 million barrels oil equivalent per day. This way, the oil and gas reserve available can meet only 43 and 167 years further. On the other hand, the utility of plastics cannot be reduced due to its wide field applications and thus results in increase in plastics waste. However, the huge amount of plastic wastes produced may be treated with suitably designed method to produce fossil fuel substitutes. The method should be superior in all respects (ecological and economical). So, a suitable process which can convert waste plastic to hydrocarbon fuel if designed and implemented then that would be a cheaper partial substitute of the petroleum without emitting any pollutants. It would also take care of hazardous plastic waste and reduce the import of crude oil. The analysis of different methods described in previous section indicate mechanical recycling is widely adapted method by different countries, however gradually the catalytic pyrolysis of plastic to fuel is gaining momentum and being adopted in different countries recently due to its efficiency over other process in all respects. In addition, this method would produce a substitute for

the fossil fuel, so be an alternate source of energy. Depletion of non-renewable source of energy such as fossil fuel at this stage demands the improvement of this technique. This sets the future trends in plastics recycling as an Industry.

## References

- [1] The compelling facts about plastics. Analysis of plastics production, demand and recovery for 2005 in Europe published in 2007 [[http://www.kunststoff-land-nrw.de/modules/kln\\_infomaterial/files/623f1d611b6ae2b.pdf](http://www.kunststoff-land-nrw.de/modules/kln_infomaterial/files/623f1d611b6ae2b.pdf)] and the compelling facts about plastics, Analysis of plastics production, demand and recovery for 2006 in Europe published in 2008 [<http://www.pvc.org/PVC.org/Media-Centre/Documents-Library/The-Compelling-Facts-about-Plastics>].
- [2] Indian Plastic Industry Review & Outlook, plastindia foundation report [[http://www.cipad.org/files/files/india\\_2006.pdf](http://www.cipad.org/files/files/india_2006.pdf)].
- [3] Mutha NH, Patel M, Premnath V. Plastics materials flow analysis for India. Resources, Conservation and Recycling 2006;47:222–44.
- [4] Gupta S, Mohan K, Prasad R, Gupta S, Kansal A. Solid waste management in India: options and opportunities. Resources Conservation and Recycling 1998;24:137–54.
- [5] Narayan P, Lindhqvist T, Tojo T. Analysing plastic waste management in India, M.Sc.(Environmental Management and Policy) Thesis, Lund, Sweden; September 2001.
- [6] Achilias DS, Roupakias C, Megalokonomos P, Lappas AA, Antonakou EV. Chemical recycling of plastic wastes made from polyethylene (LDPE and HDPE) and polypropylene (PP). Journal of Hazardous Materials 2007;149:536–42.
- [7] Scott DS, Czernik SR, Piskorz J, Radlein DSAG. Fast pyrolysis of plastic. Energy and Fuels 1990;4:407–11.
- [8] Miskolczi N, Bartha L, Deak G, Jover B. Thermal degradation of municipal plastic waste for production of fuel-like hydrocarbons. Polymer Degradation and Stability 2004;86:357–66.
- [9] Uemura Y, Baba K, Ohe H, Ohzuno Y, Hatate Y. Catalytic decomposition of hydrocarbon into hydrogen and carbon in a spouted-bed reactor as the second-stage reactor of a plastic recycling process. The Journal of Material Cycles and Waste Management 2003;5:94–7.
- [10] Buekens AG, Huang H. Catalytic plastics cracking for recovery of gasoline-range hydrocarbons from municipal plastic wastes. Resources Conservation and Recycling 1998;23:163–81.
- [11] Balakrishnan RK, Guria C. Thermal degradation of polystyrene in the presence of hydrogen by catalyst in solution. Polymer Degradation and Stability 2007;92:1583–91.
- [12] Waste Management in China: Issues and recommendations; May 2005 [<http://siteresources.worldbank.org/INTEAPREGTOPURBDEV/Resources/China-Waste-Management1.pdf>].
- [13] Toward an Era of Environmental Revolution, Japan [<http://www.env.go.jp/ewp/wpaper/2004/02.pdf>].
- [14] Plastic Wastes: Resource Recovery and Recycling in Japan. Tokyo: Plastic Waste Management Institute; 1985 <<http://www.google.com/>>.
- [15] Bahr A, Kozmiensky T. The sorting of plastic wastes. Berlin Freitag Verlag: International Recycling Congress; 1979. p. 1202–10.
- [16] Luo G, Suto T, Yasu S, Kato K. Catalytic degradation of high density polyethylene and polypropylene into liquid fuel in a powder-particle fluidized bed. Polymer Degradation and Stability 2007;70:97–102.
- [17] Miskolczi N, Bartha L, Angyal A. High energy containing fractions from plastic wastes by their chemical recycling. Macromolecules Symposium 2006;245–246:599–606.
- [18] Delattre C, Forissiera M, Pitault I. Improvement of the microactivity test for kinetic and deactivation studies involved in catalytic cracking. Chemical Engineering Science 2001;56(4):1337–45.
- [19] Garforth AA, Ali S, Martínez JH, Akah A. Feedstock recycling of polymer wastes. Current Opinion in Solid State and Materials Science 2004;8(6):419–25.
- [20] Scott G. Green polymers. Polymer Degradation and Stability 2000;68:1–7.
- [21] Mantia PL. Handbook of plastics recycling. Francesco; 2002. ISBN: 1859573258, 9781859573259.
- [22] Scott G. Polymers and the environment. Royal Society of Chemistry; 1999 978-1-84755-172-6 [online].
- [23] Scott G. Antioxidants in science, technology, medicine and nutrition. Chichester: Albion Publishing; 1997 [chapter 3].
- [24] Scott G. Antioxidant control of polymer biodegradation. In: 5th international workshop on biodegradable plastics and polymers; Macromolecular Symposia 1998.
- [25] Scott G. Abiotic control of polymer biodegradation. Trends in Polymer Science 1997;5:361–8.
- [26] Scott Gerald. Degradable polymers: principles and applications, 2<sup>nd</sup> ed., Springer; 2002. ISBN: 1402007906, 9781402007903.
- [27] Plastics recycling information sheet, <http://www.wasteonline.org.uk/resources/InformationSheets/Plastics.htm>.
- [28] Environment Australia, Incineration and Dioxins: Review of Formation Processes, consultancy report prepared by Environmental and Safety Services for Environment Australia, Commonwealth Department of the Environment and Heritage, Canberra; 1999 [<http://www.environment.gov.au/settlements/publications/chemicals/dioxins/pubs/incineration-review.pdf>].
- [29] Yamamoto T, Isaka K, Sato H, Matsukura Y, Ishida H. Gasification and smelting system using oxygen blowing for municipal waste. ISIJ International 2000;40(3):260–5.
- [30] Murata K, Sato K, Sakata Y. Effect of pressure on thermal degradation of polyethylene. Journal of Analytical and Applied Pyrolysis 2004;71(2):569–89.
- [31] Sorum L, Gronli MG, Hustad JE. Pyrolysis characteristics and kinetics of municipal solid wastes. Fuel 2001;80(9):1217–27.
- [32] Faravelli T, Pincioli M, Pisano F, Bozzano G, Dente M, Ranzi E. Thermal degradation of polystyrene. Journal of Analytical and Applied Pyrolysis 2001;60(1):103–21.
- [33] Demirbas A. Pyrolysis of municipal plastic waste for recovery of gasoline-range hydrocarbons. Journal of Analytical and Applied Pyrolysis 2004;72:97–102.
- [34] Mastral FJ, Esperanza E, García P, Juste M. Pyrolysis of high-density polyethylene in a fluidised bed reactor. Influence of the temperature and residence time. Journal of Analytical and Applied Pyrolysis 2002;63(1):1–15.
- [35] Garforth A, Lin YH, Sharratt PN, Dwyer J. Production of hydrocarbons by catalytic degradation of high density polyethylene in a laboratory fluidised-bed reactor. Applied Catalysis A General 1998;169(2):331–42.
- [36] Cha WS, Kim SB, McCoy BJ. Study of polystyrene degradation using continuous distribution kinetics in a bubbling reactor. Korean Journal of Chemical Engineering 2002;19(2):239–45.
- [37] Dolezal Z, Pacakova V, Kovarova J. The effects of controlled aging and blending of low- and high-density polyethylenes, polypropylene and polystyrene on their thermal degradation studied by pyrolysis gas chromatography. Journal of Analytical and Applied Pyrolysis 2001;57(2):177.
- [38] Kim SS, Kim S. Pyrolysis characteristics of polystyrene and polypropylene in a stirred batch reactor. Chemical Engineering Journal 2004;98(1–2):53–60.
- [39] Woo OS, Ayala N, Broadbelt LJ. Mechanistic interpretation of base-catalyzed depolymerization of polystyrene. Catalysis Today 2000;55(1–2):161–71.
- [40] Woo OS, Broadbelt LJ. Recovery of high-valued products from styrene-based polymers through co processing: experiments and mechanistic modeling. Catalysis Today 1998;40:121–40.
- [41] Chan JH, Balke ST. The thermal degradation kinetics of polypropylene: Part III. Thermogravimetric analyses. Polymer Degradation and Stability 1997;57(2):135–49.
- [42] Hayashi J, Nakahara J, Kusakabe K, Morooka S. Pyrolysis of polypropylene in the presence of oxygen. Fuel Processing Technology 1998;55(3):265–75.
- [43] Jakab E, Varhegyi G, Faix O. Thermal decomposition of polypropylene in the presence of wood-derived materials. Journal of Analytical and Applied Pyrolysis 2000;56(2):273.
- [44] Kaminsky W. Thermal recycling of polymers. Journal of Analytical and Applied Pyrolysis 1985;8:439–48.
- [45] Kaminsky W, Predel M, Sadiki A. Feedstock recycling of polymers by pyrolysis in a fluidised bed. Polymer Degradation and Stability 2004;85(3):1045–50.
- [46] Kiang JKY, Uden PC, Chien JCW. Polymer reactions-Part VII: Thermal pyrolysis of polypropylene. Polymer Degradation and Stability 1980;2(2):113–27.
- [47] Lattimer RP. Direct analysis of polypropylene compounds by thermal desorption and pyrolysis-mass spectrometry. Journal of Analytical and Applied Pyrolysis 1993;26(2):65.
- [48] Marcilla A, Beltran M, Conesa JA. Catalyst addition in polyethylene pyrolysis—Thermogravimetric study. Journal of Analytical and Applied Pyrolysis 2001;58:117–26.
- [49] Murata K, Hirano Y, Sakata Y, Azhar Uddin M. Basic study on a continuous flow reactor for thermal degradation of polymers. Journal of Analytical and Applied Pyrolysis 2002;65(1):71–90.
- [50] Onu P, Vasile C, Ciocilteu S, Iojoiu S, Darie H. Thermal and catalytic decomposition of polyethylene and polypropylene. Journal of Analytical and Applied Pyrolysis 1999;49(1–2):145–53.
- [51] Ranzi E, Dente M, Faravelli T, Bozzano G, Fabini S, Nava R, et al. Kinetic modeling of polyethylene and polypropylene thermal degradation. Journal of Analytical and Applied Pyrolysis 1997;40–41:305–19.
- [52] Seth D, Sarkar A. Thermal pyrolysis of polypropylene: effect of reflux-condenser on the molecular weight distribution of products. Chemical Engineering Science 2004;59(12):2433–45.
- [53] Tsuchiya Y, Sumi K. Thermal decomposition products of polypropylene. Journal of Polymer Science 1969;7:1599–607.
- [54] Bockhorn H, Hornung A, Hornung U, Schwallier D. Kinetic study on the thermal degradation of polypropylene and polyethylene. Journal of Analytical and Applied Pyrolysis 1999;48(2):93–109.
- [55] Audisio G. Catalytic thermal degradation of polymers: degradation of polypropylene. Journal of Analytical and Applied Pyrolysis 1984;7(1–2):83.
- [56] Scott DS, Czernik SR, Piskorz J, Radlein AG. Fast pyrolysis of plastic wastes. Energy & Fuels 1990;4:407–11.
- [57] Sakata Y, Uddin MA, Koizumi K, Murata K. Thermal degradation of polyethylene mixed with poly(vinyl chloride) and poly(ethyleneterephthalate). Polymer Degradation and Stability 1996;53(1):111–7.
- [58] McCaffrey WC, Kamal MR, Cooper DG. Thermolysis of polyethylene. Polymer Degradation and Stability 1995;47(1):133–9.
- [59] Songip AR. Test to screen catalysts for reforming heavy oil from waste plastics. Applied Catalysis B Environmental 1993;2(2–3):153–64.
- [60] Joo HS, Guin JA. Continuous upgrading of a plastics pyrolysis liquid to an environmentally favorable gasoline range product. Fuel Processing Technology 1998;57:25–40.

- [61] Serrano DP, Aguado J, Escola M, Garagorri E. Performance of a continuous screw kiln reactor for the thermal and catalytic conversion of polyethylene-lubricating oil base mixtures. *Applied Catalysis B Environmental* 2003;44(2):95–105.
- [62] Ohkita H, Nishiyama R, Tochiwara Y, Mizushima T, Kakuta N, Morioka Y. Acid properties of silica-alumina catalysts and catalytic degradation of polyethylene. *Industrial & Engineering Chemistry Research* 1993;32(12):3112–6.
- [63] Ding WB, Liang J, Anderson LL. Thermal and catalytic degradation of high density polyethylene and commingled post-consumer plastic waste. *Fuel Processing Technology* 1997;51(1–2):47–62.
- [64] Park DW, Hwang EY, Kim JR, Choi JK, Kim YA, Woo HC. Catalytic degradation of polyethylene over solid acid catalysts. *Polymer Degradation and Stability* 1999;65(2):193–8.
- [65] Lee SY. Catalytic degradation of polystyrene over natural clinoptilolite zeolite. *Polymer Degradation and Stability* 2001;74(2):297–305.
- [66] Lee SY, Yoon JH, Kim JR, Park DW. Catalytic conversion of low-density polyethylene using a continuous screw kiln reactor. *Catalysis Today* 2002;75(1–4):257–62.
- [67] Park JJ, Park JW, Park J, Kim DC. Characteristics of LDPE pyrolysis. *Korean Journal of Chemical Engineering* 2002;19(4):658–62.
- [68] Hwang EY, Choi JK, Kim DH, Park DW. Catalytic degradation of polypropylene I. Screening of catalysts. *Korean Journal of Chemical Engineering* 1998;15(4):434–8.
- [69] Hwang EY, Kim JR, Choi JK, Woo HC, Park DW. Performance of acid treated natural zeolites in catalytic degradation of polypropylene. *Journal of Analytical and Applied Pyrolysis* 2002;62(2):351–64.
- [70] Bagri R, Williams PT. Fluidised-bed catalytic pyrolysis of polystyrene. *Journal of the Institute of Energy* 2002;75(505):117–23.
- [71] Kim JR, Yoon JH, Park DW. Catalytic recycling of the mixture of polypropylene and polystyrene. *Polymer Degradation and Stability* 2002;76(1):61–7.
- [72] Aguado J, Serrano DP, Escola JM, Garagorri E, Fernández JA. Catalytic conversion of polyolefins into fuels over Zeolite beta. *Polymer Degradation and Stability* 2000;69(1):11–6.
- [73] Seo YH, Lee KH, Shin DH. Investigation of catalytic degradation of high-density polyethylene by hydrocarbon group type analysis. *Journal of Analytical and Applied Pyrolysis* 2003;70(2):383–98.
- [74] Beltrame PL, Carniti P, Audisio G, Bertini F. Catalytic degradation of polymers: Part II. Degradation of polyethylene. *Polymer Degradation and Stability* 1989;26(3):209–15.
- [75] Sakata Y, Uddin MA, Muto A. Degradation of polyethylene and polypropylene into fuel oil by using solid acid and non-acid catalysts. *Journal of Analytical and Applied Pyrolysis* 1999;51(1–2):135–55.
- [76] Alka Zadgaonkar. Conversion of Waste Plastic into Liquid Hydrocarbons/Energy—A major breakthrough in the arena of non-conventional sources of energy. Information Brochure and Technical Write-Up. <http://www.plastic2-petrol.com/AlkaZadgaonkar.html>.
- [77] Scheirs J, Kaminsky W. Feedstock recycling of waste plastics. John Wiley & Sons, Ltd.; 2006.
- [78] Cullis CF, Hirschler MM. The Combustion of Organic Polymers. Oxford Clarendon Press; 1981.
- [79] Singh B, Sharma N. Mechanistic implications of plastic degradation. *Polymer Degradation and Stability* 2008;93:561–84.
- [80] Corma A. Inorganic solid acids and their use in acid-catalyzed hydrocarbon reactions. *Chemistry Reviews* 1995;95(3):559–614.
- [81] Lonyi F, Valyon J. On the interpretation of the NH<sub>3</sub>-TPD patterns of H-ZSM-5 and H-mordenite. *Microporous and Mesoporous Materials* 2001;47:293–301.
- [82] Armatori L. FTIR study of the interaction of some branched aliphatic molecules with the external and internal sites of H-ZSM5 Zeolite. *Chemical Physics Letters and Chemical Physics* 2000;2:3341–8.
- [83] Cerqueira HS, Ayrault P, Datka J, Guisnet M. Influence of coke on the acid properties of a USHY zeolite. *Microporous and Mesoporous Materials* 2000;38:197–205.
- [84] Topsoe NY, Pedersen K, Derouane EG. Infrared and temperature-programmed desorption study of the acidic properties of ZSM-5-type zeolites. *Journal of Catalysis* 1981;70(1):41–5.
- [85] Venuto P, Landis P. Zeolite catalysis in synthetic organic chemistry. *Advances in Catalysis* 1968;18:259–67.
- [86] Sekine Y, Fujimoto K. Catalytic degradation of PP with an Fe/activated carbon catalyst. *Journal of Material Cycles and Waste Management* 2003;5:107–12.
- [87] Wall LL, Madorsky SL, Brown DW, Straus S. The depolymerization of polymethylene and polyethylene. *Journal of the American Chemical Society* 1954;76:343–7.
- [88] Lee KH, Shin DH. Catalytic degradation of waste polyolefinic polymers using spent FCC catalyst with various experimental variables. *Korean Journal of Chemical Engineering* 2003;20(1):89–92.
- [89] Walendziewski J. Engine fuel derived from waste plastics by thermal treatment. *Fuel* 2002;81(4):473–81.
- [90] Serrano DP, Aguado J, Escola JM, Garagorri J, Rodriguez JM, Morselli L, et al. Feedstock recycling of agriculture plastic film wastes by catalytic cracking. *Applied Catalysis B Environmental* 2004;49(4):257–65.
- [91] Hernandez MD, Garcia AN, Marcilla A. Study of the gases obtained in thermal and catalytic flash pyrolysis of HDPE in a fluidized bed reactor. *Journal of Analytical and Applied Pyrolysis* 2005;73(2):314–22.
- [92] Wong HW, Broadbel LJ. Tertiary resource recovery from waste polymers via pyrolysis: neat and binary mixture reactions of polypropylene and polystyrene. *Industrial & Engineering Chemistry Research* 2001;40(22):4716–23.
- [93] Lin YH, Yang MH. Catalytic reactions of post-consumer polymer waste over fluidised cracking catalysts for producing hydrocarbons. *Journal of Molecular Catalysis A Chemical* 2005;231(1–2):113–22.
- [94] Marcilla A, Garcia-Quesada JC, Sanchez S, Ruiz R. Study of the catalytic pyrolysis behavior of polyethylene-polypropylene mixtures. *Journal of Analytical and Applied Pyrolysis* 2005;74(1–2):387–92.
- [95] Lee KH, Shin DH, Seo YH. Liquid-phase catalytic degradation of mixtures of waste high-density polyethylene and polystyrene over spent FCC catalyst. Effect of mixing proportions of reactants. *Polymer Degradation and Stability* 2004;84(1):123–7.
- [96] Bhaskar T, Kaneko J, Muto A, Sakata Y, Jakab E, Matsui T, et al. Pyrolysis studies of PP/PE/PS/PVC/HIPS-Br plastics mixed with PET and dehalogenation (Br, Cl) of the liquid products. *Journal of Analytical and Applied Pyrolysis* 2004;72(1):27–33.
- [97] Manos G, Garforth A, Dwyer J. Catalytic degradation of high-density polyethylene on an ultrastable-Y Zeolite. Nature of initial polymer reactions, pattern of formation of gas and liquid products, and temperature effects. *Industrial & Engineering Chemistry Research* 2000;39:1203–8.
- [98] Lee KH, Noh NS, Shin DH, Seo Y. Comparison of plastic types for catalytic degradation of waste plastics into liquid product with spent FCC catalyst. *Polymer Degradation and Stability* 2002;78(3):539–44.
- [99] Marcilla A, Gomez A, Garcia AN, Olaya MM. Kinetic study of the catalytic decomposition of different commercial polyethylenes over an MCM-41 catalyst. *Journal of Analytical and Applied Pyrolysis* 2002;64(1):85–101.
- [100] de la Puente G, Sedran U. Recycling polystyrene into fuels by means of FCC: performance of various acidic catalysts. *Applied Catalysis B Environmental* 1998;19(3–4):305–11.
- [101] Mertinkat J, Predel K, Kaminsky W. Cracking catalysts used as fluidized bed material in Hamburg pyrolysis process. *Journal of Analytical and Applied Pyrolysis* 1999;49:87–95.
- [102] De la Puente G, Arandes JM, Sedran U. Recycled plastics in FCC feedstocks: specific contributions. *Industrial and Engineering Chemistry Research* 1997;36:4530–4.
- [103] Faravelli T, Bozzano G, Colombo M, Ranzi E, Dente M. Kinetic modeling of thermal degradation of polyethylene and polystyrene mixtures. *Journal of Analytical and Applied Pyrolysis* 2003;70:761–77.
- [104] Pinto F, Costa P, Cabrita G. Pyrolysis of plastic wastes 2. Effect of catalyst on product yield. *Journal of Analytical and Applied Pyrolysis* 1999;51:57–71.
- [105] Aguado J, Serrano DP, Sotelo JL, Van Grieken R, Escola JM. Influence of the operating variables on the catalytic conversion of a polyolefin mixture over HZSM-41 and nanosized HZSM-5. *Industrial & Engineering Chemistry Research* 2001;40(24):5696–704.
- [106] Zeng GM, Yuan XZ, Yin YY, Hu TJ, Yan G. Manufacture of liquid fuel by catalytic cracking waste plastics in a fluidized bed. *Energy Sources* 2003;25(6):577–90.
- [107] Akpanudoh NS, Gobin K, Manos G. Catalytic degradation of plastic waste to liquid fuel over commercial cracking catalysts: effect of polymer to catalyst ratio/acidity content. *Journal of Molecular Catalysis A Chemical* 2005;235(1–2):67–73.
- [108] Karagoz S, Karagoz S, Yanik J, Ucar S, Saglam M, Song C. Catalytic and thermal degradation of high-density polyethylene in vacuum gas oil over non-acidic and acidic catalysts. *Applied Catalysis A General* 2003;242(1):51–62.
- [109] Luo GH. Catalytic degradation of high density polyethylene and polypropylene into liquid fuel in a powder-particle fluidized bed. *Polymer Degradation and Stability* 2000;70(1):97–102.
- [110] Anders G, Burkhardt I, Illgen U, Schultz IW, Scheve J. The influence of HZSM-5 zeolite on the product composition after cracking of high boiling hydrocarbon fractions. *Applied Catalysis A General* 1990;62(1):271–8.
- [111] Corma A, Planellas J, Sanchez-Marin J, Thomas F. The role of different types of acid site in the cracking of alkanes on zeolite catalysts. *Journal of Catalysis* 1985;93(1):30–7.
- [112] Manos G, Garforth A, Dwyer J. Catalytic degradation of high-density polyethylene over different zeolitic structures. *Industrial & Engineering Chemistry Research* 2000;39(5):1198–202.
- [113] Mordt RC, Fields R, Dwyer J. Thermolysis of low density polyethylene catalysed by zeolites. *Journal of Analytical and Applied Pyrolysis* 1994;29(1):45.
- [114] Aguado J, Sotelo JL, Serrano DP, Calles JA, Escola JM. Catalytic conversion of polyolefins into liquid fuels over MCM-41: Comparison with ZSM-5 and amorphous Si(O)<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. *Energy & Fuels* 1997;11(6):1225–31.
- [115] Marcilla A, Gomez A, Reyes-Labarta JA, Giner A. Catalytic Pyrolysis of polypropylene using MCM-41: kinetic model. *Polymer Degradation and Stability* 2003;80(2):233–40.
- [116] Pierella LB, Renzini S, Anunziata OA. Catalytic degradation of high density polyethylene over microporous and mesoporous materials. *Microporous and Mesoporous Materials* 2005;81(1–3):155–9.
- [117] Anunziata OA, Pierella LB. Conversion of polyethylene into aromatic hydrocarbons using MEL and BEA zeolites. *Studies in Surface Science and Catalysis* 1999;125:481–8.
- [118] Garforth AA, Lin YH, Sharratt PN, Dwyer J. Catalytic polymer degradation for producing hydrocarbons over Zeolites. *Studies in Surface Science and Catalysis* 1999;121:197–202.
- [119] Songip AR, Masuda T, Kuwahara H, Hashimoto K. Kinetic studies for catalytic cracking of heavy oil from waste plastics over REY Zeolite. *Energy and Fuels* 1994;8:131–5.



- [120] You YS, Shim JS, Kim JH, Seo GI. Liquid-phase degradation of polyethylene wax over mordenite catalysts with different Si-Al molar ratios. *Catalysis Letters* 1999;59(2–4):221–7.
- [121] Seo YH, Lee KH, Shin DH. Investigation of catalytic degradation of high density, polyethylene by hydrocarbon group type analysis. *Journal of Analytical and Applied Pyrolysis* 2003;70:383–98.
- [122] Mastral JF, Berruoco C, Gea M, Ceamanos J. Catalytic degradation of high density polyethylene over nanocrystalline HZSM-5 Zeolite. *Polymer Degradation and Stability* 2006;91:3330–8.
- [123] Degnan TF. Applications of zeolites in petroleum refining. *Topics in Catalysis* 2000;13:349–56.
- [124] Habib Jr ET, Gilson JP. Advances in fluid catalytic cracking. *Catalytic Science Series Zeolites for Cleaner Technologies*, vol. 3. 2002. pp. 105–130.
- [125] Sivasanker S. Catalysis in petroleum refining. *Catalysis* 2002;362–76.
- [126] Manos G, Isman Y, Papayannakos YN, Gangas NH. Catalytic cracking of polyethylene over clay catalysts. Comparison with an ultrastable Y Zeolite. *Industrial & Engineering Chemistry Research* 2001;40:2220–5.
- [127] Siauw HN, Seoud H, Stanculescu M, Sugimoto Y. Conversion of polyethylene to transportation fuels through pyrolysis and catalytic cracking. *Energy & Fuels* 1995;9:735–42.
- [128] Kima JR, Kima YA, Yoona JH, Parka DW, Woob HC. Catalytic degradation of polypropylene: effect of dealumination of clinoptilolite catalyst. *Polymer Degradation and Stability* 2002;75:287–94.
- [129] Grieken RV, Serrano DP, Aguado J, Garcia R, Rojo C. Thermal and catalytic cracking of polyethylene under mild conditions. *Journal of Analytical and Applied Pyrolysis* 2001;58:127–42.
- [130] Sharratt PN, Lin YH, Garforth AA, Dwyer J. Investigation of the catalytic pyrolysis of high-density polyethylene over a HZSM-5 catalyst in a laboratory fluidized-bed reactor. *Industrial & Engineering Chemistry Research* 1997;36:5118–24.
- [131] Azhar uddin M, Koizumi K, Murata K, Sakata Y. Thermal and catalytic degradation of structurally different types of polyethylene into fuel oil. *Polymer Degradation and Stability* 1997;56:37–44.
- [132] Sakata Y, Uddin MA, Muto A. Degradation of polyethylene and polypropylene into fuel oil by using solid acid and non-acid catalysts. *Journal of Analytical and Applied Pyrolysis* 1999;51:135–55.
- [133] Serrano DP, Aguado J, Escola JM. Catalytic cracking of a polyolefin mixture over different acid solid catalysts. *Industrial & Engineering Chemistry Research* 2000;39:1177–84.
- [134] Aguado J, Serrano DP, Miguel GS, Castro MC, Madrid S. Feedstock recycling of polyethylene in a two-step thermo-catalytic reaction system. *Journal of Analytical and Applied Pyrolysis* 2007;79:415–23.
- [135] Miskolczi N, Bartha L, Deak G. Thermal degradation of polyethylene and polystyrene from the packaging industry over different catalysts into fuel-like feed stocks. *Polymer Degradation and Stability* 2006; 91:517–26.
- [136] Chung SH, Park JJ, Jeon SG, Kim DC. Pyrolysis of waste plastics using synthesized catalysts from fly ash. *Journal of Industrial and Engineering Chemistry* 2003;9(2):181–7.
- [137] Shah J, Jan MR, Hussain Z. Catalytic pyrolysis of low-density polyethylene with lead sulfide into fuel oil. *Polymer Degradation and Stability* 2005;87:329–33.
- [138] Zhibo Z, Nishio S, Morioka Y, Ueno A, Ohkita H, Tochihara Y, et al. Thermal and chemical recycle of waste polymers. *Catalysis Today* 1996;29:303–8.
- [139] You YS, Kim JH, Seo G. Liquid-phase catalytic degradation of polyethylene wax over MFI zeolites with different particle sizes. *Polymer Degradation and Stability* 2000;70(3):365–71.
- [140] Serrano D, Aguado J, Escola J, Rodriguez J. Nanocrystalline ZSM-5: a highly active catalyst for polyolefin feedstock recycling. *Studies in Surface Science and Catalysis* 2002;142:77–84.
- [141] Takuma K, Uemichi Y, Sudioka M, Ayame A. A novel technology for chemical recycling of low-density polyethylene by selective degradation into lower olefins using h-borosilicate as a catalyst. *Chemistry Letters* 2001;4:288–9.
- [142] De Lasa HI, Riser simulator for catalytic cracking studies. *US Patent* 5,102,628; 1992.
- [143] Puente DL, Klocker GC, Sedran U. Conversion of waste plastics into fuels—Recycling polyethylene in FCC. *Applied Catalysis B Environmental* 2002;36(4):279–85.
- [144] Mahgoub KA, Al-Khattaf S. Catalytic cracking of hydrocarbons in a riser simulator: The effect of catalyst accessibility and acidity. *Energy & Fuels* 2005;19(2):329–38.
- [145] Miskolczi N, Bartha L, Deák G, Jóver B, Kalló D. Thermal and thermo-catalytic degradation of high-density polyethylene waste. *Journal of Analytical and Applied Pyrolysis* 2004;72(2):235–42.
- [146] Mastellone ML, Arena U. Fluidized bed pyrolysis of a recycled polyethylene. *Polymer Degradation and Stability* 2002;76(3):479–87.
- [147] Liu Y, Qian J, Wang J. Pyrolysis of polystyrene waste in a fluidized-bed reactor to obtain styrene monomer and gasoline fraction. *Fuel Processing Technology* 2000;63(1):45.
- [148] Plastics Recycling—Economic & Ecological Options, vol. 4, no. 4; October–December 2006 <[http://icpeenviis.nic.in/enviis\\_newsletter/Enviis\\_Oct\\_Dec06](http://icpeenviis.nic.in/enviis_newsletter/Enviis_Oct_Dec06)>.
- [149] Waste Plastics into Oil <<http://www.i-sis.org.uk/WPIO.php>> (ISIS Press Release 29/11/05).
- [150] Zhang GH, Zhu JF, Okuwaki A. Prospect and current status of recycling waste plastics and technology for converting them into oil in China. *Resources Conservation and Recycling* 2007;50(3):231–9.
- [151] Chinese Invent Technology to Convert Plastics Back into Oil <[http://www.lo-calplanet.ie/index.php?option=com\\_content&task=view&id=197&Itemid=>](http://www.lo-calplanet.ie/index.php?option=com_content&task=view&id=197&Itemid=>)>.
- [152] Waste Plastics to Oil Technology Overview <[http://www.environmental-technologysystems.ltd.uk/tech\\_ov.php](http://www.environmental-technologysystems.ltd.uk/tech_ov.php)>.
- [153] Converting Plastic Waste into Petrol <<http://www.tribuneindia.com/2003/20030928/spectrum/main4.htm>>.
- [154] A Wand that Converts Plastic Waste to Fuel <<http://mangalorean.com/news.php?newstype=local&newsid=38714>>.
- [155] Recycling company building \$50m plastic-to-fuel plant <<http://www.asiaone.com/Business/News/SME%2BCentral/Story/A1Story20071221-42041.html>>.
- [156] Recycling of plastics <<http://www.spra.org.uk/sprafam1.html>>.